Total Maximum Daily Load
for Mercury

in McPhee & Narraguinnep Reservoirs, Colorado

REVIEW DRAFT

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COLORADO DEPARTMENT OF PUBLIC HEALTH AND ENVIRONMENT

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Table of Contents

CHANGE this to the fish consumption advisory position paper??????

DO WE need this in the final TMDL?????

List of Tables

List of Figures

Executive Summary

The Colorado Department of Public Health and the Environment (CDPHE) has identified McPhee and Narraguinnep Reservoirs as not supporting their designated uses due to the presence of elevated fish tissue concentrations of mercury that have resulted in issuing Fish Consumption Advisories. Mercury concentrations at the levels observed present a significant health risk to persons who consume listed fish from these Reservoirs. Ambient water quality criteria for concentrations of mercury in water have not been exceeded; however, the physical and chemical characteristics of the lakes lead to a situation in which mercury builds up in fish tissue to levels that present a risk to human health. Because McPhee and Narraguinnep Reservoirs do not support their designated uses, CDPHE will develop a Total Maximum Daily Load (TMDL) for mercury loading to the lake. The TMDL is a mechanism established in the Clean Water Act for situations in which water quality impairment has not been mitigated by imposition of the minimum required levels of technology-based effluent limits on permitted point sources. The U.S. Environmental Protection Agency (EPA), Region 8, is supporting CDPHE in the development of this TMDL. Support provided by Region 8 includes this technical assessment of mercury loads and potential allocations.

The TMDLs for McPhee and Narraguinnep Reservoirs are linked because the two waterbodies are intimately linked. Most of the water stored in Narraguinnep is diverted from McPhee Reservoir. As a result, mercury concentrations in Narraguinnep depend in part on mercury concentrations in McPhee Reservoir, and management to address water quality problems in Narraguinnep must also address mercury loading to McPhee.

The TMDL consists of an allocation of the available loading capacity of a waterbody (the maximum rate of loading that would be consistent with achieving designated uses) to point sources, nonpoint sources, and a margin of safety. This TMDL assessment estimates that the loading capacity of McPhee Reservoir is approximately 2,592 grams of mercury per year. The loading capacity of the smaller Narraguinnep Reservoir is estimated to be 39 grams of mercury per year. Within the upland watersheds that contribute flow to the Reservoirs there are no permitted point sources of mercury discharge. There are, however, significant loads of mercury to McPhee Reservoir that derive from past mining activities. In addition, there are nonpoint or diffuse loads of mercury to both Reservoirs that derive from naturally occurring background in local rocks, atmospheric deposition, and other sources. For Narraguinnep Reservoir, the direct deposition of atmospheric mercury to the lake surface appears to be a significant factor in the elevation of mercury concentrations in fish tissue. These atmospheric loads derive from both distant and nearby sources, and appear to be enhanced by emissions from coal-fired power plants located south and west of the Reservoir.

This technical analysis contains a proposal for potential allocations that include reductions in both the watershed runoff loading of mercury from mining districts in the McPhee watershed and reductions in the atmospheric deposition of mercury. Reduction in atmospheric loads will be needed to meet water quality standards in Narraguinnep, regardless of the degree of control achieved on watershed loads. Because there is considerable uncertainty in the estimation of the proposed allocations, continued monitoring to assess progress toward achieving safe fish tissue concentrations in the Reservoirs is also strongly recommended. .

1. Introduction and Problem Statement

1.1 Description of TMDL Process

High-quality water is an extremely valuable commodity in Colorado. Water quality standards are established to protect the designated uses of Colorado's waters. When states and local communities identify problems in meeting water quality standards, a Total Maximum Daily Load (TMDL) can be part of a plan to fix the water quality problems. The purpose of this TMDL is to provide an estimate of pollutant loading reductions needed to restore the beneficial uses of McPhee and Narraguinnep Reservoirs.

Section 303(d) of the Clean Water Act (CWA) requires states to identify the waters for which the effluent limitations required under the National Pollutant Discharge Elimination System (NPDES) or any other enforceable limits are not stringent enough to meet any water quality standard adopted for such waters. The states must also rank these impaired waterbodies by priority, taking into account the severity of the pollution and the uses to be made of the waters. Lists of prioritized impaired waterbodies are known as the "303(d) lists" and must be submitted to EPA every two years.

A TMDL represents the total loading rate of a pollutant that can be discharged to a waterbody and still meet the applicable water quality standards. The TMDL can be expressed as the total mass or quantity of a pollutant that can enter the waterbody within a unit of time. In most cases, the TMDL determines the allowable loading capacity for a constituent and divides it among the various contributors in the watershed as wasteload (i.e., point source discharge) and load (i.e., nonpoint source) allocations. The TMDL also accounts for natural background sources and provides a margin of safety. For some nonpoint sources it might not be feasible or useful to derive an allocation in mass per time units. In such cases, a percent reduction in pollutant discharge may be proposed.

TMDLs must include specific information to be approved by USEPA, Region 8. This information can be summarized in the following seven elements:

1. **Plan to meet state water quality standards:** The TMDL includes a study and a plan for the specific water and pollutants that must be addressed to ensure that applicable water quality standards are attained.

2. **Describe quantified water quality goals, targets, or endpoints:** The TMDL must establish numeric endpoints for the water quality standards, including beneficial uses to be protected, as a result of implementing the TMDL. This often requires an interpretation that clearly describes the linkage(s) between factors impacting water quality standards.

3. **Analyze/account for all sources of pollutants:** All significant pollutant sources are described, including the magnitude and location of sources.

4. **Identify pollution reduction goals:** The TMDL plan includes pollutant reduction targets for all point and nonpoint sources of pollution.

5. **Describe the linkage between water quality endpoints and pollutants of concern:** The TMDL must explain the relationship between the numeric targets and the pollutants of concern. That is, do the recommended pollutant load allocations exceed the loading capacity of the receiving water?

6. **Develop Margin of Safety that considers uncertainties, seasonal variations, and critical conditions:** The TMDL must describe how any uncertainties regarding the ability of the plan to meet water quality standards have been addressed. The plan must consider these issues in its recommended pollution reduction targets.

7. **Include an appropriate level of public involvement in the TMDL process:** This is usually achieved by publishing public notice of the TMDL, circulating the TMDL for public comment, and holding public meetings in local communities. Public involvement must be documented in the state's TMDL submittal.

1.2 Waterbody Name and Location

The waterbodies of concern I nths TMDL are McPhee and Narraguinnep Reservoirs in Montezuma County, southwestern Colorado. The general characteristics of the two Reservoirs and their watersheds are described in Tetra Tech (2000) and are summarized only briefly here. McPhee Reservoir is an impoundment of the Dolores River (USGS Hydrologic Cataloging Unit [HUC] 14030002) operated by the Bureau of Reclamation in Montezuma County, Colorado. The Reservoir was completed in 1986. It has a surface area of 4,470 acres and a storage capacity of 381,051 acre-feet at 6,924 ft MSL.

Narraguinnep Reservoir, a privately owned impoundment constructed in 1907. It has a surface area of 625 acres at full pool and a storage capacity of 18,960 acre-feet at 6,680 ft MSL. The watershed for Narraguinnep Reservoir lies in a different HUC (14080202) than McPhee Reservoir. However, the majority of water in Narraguinnep is supplied by McPhee Reservoir via interbasin transfer.

The locations of the two watersheds are shown in Figure 1-1. A detailed view of the McPhee and Narraguinnep watersheds is provided in Figure 1-2.

1.3 Geographic Coverage of the TMDL

Water quality and beneficial uses are documented as impaired only within the Reservoirs themselves. Mercury loads, however, arise within the entire upstream watershed area, including sources from mining activities, soil background, and atmospheric deposition. Therefore, the geographic coverage of the TMDL is the entire upstream drainage area of the Reservoirs, including portions of Montezuma and Dolores Counties, Colorado. In addition, consideration is given to atmospheric transport of mercury from outside the watershed.

The TMDL for Narraguinnep Reservoir is combined with that for McPhee Reservoir because most of the water supplying Narraguinnep, as well as a substantial portion of the mercury load, is derived from McPhee. Thus, mitigation strategies for the two Reservoirs should be linked. The small direct drainage to Narraguinnep Reservoir within HUC 14080202 is also included in the analysis.

1.4 TMDL Priority and Targeting

The McPhee Reservoir portion of the waterbody segment Dolores River from Bear Creek to Bradfield Ranch Bridge appears on both the 1998 303(d) list and the 2000 303(d) list as high priority for development of a mercury TMDL (COSJDO04L). Similarly, Narraguinnep Reservoir is also listed as high priority for development of a mercury TMDL (COSJLP08L). The 2000 303(d) list targets these watersheds for TMDL development prior to June 2002. The development of this TMDL is consistent with the priority and target schedule assigned to these watersheds.

1.5 Health Effects of Mercury

Colorado's Fish Consumption Advisory program is designed to protect people in the state that consume fish from local waterbodies from the ill-health effects of mercury. The most toxic type of mercury to humans is the organic form, methylmercury. Unfortunately, methylercury is the predominant form found in fish tissue and consumption of fish is thought to be the primary pathway by which humans are exposed to mercury (cite EPA……). The two organ systems most likely affected by methylmercury are the central nervous system and the kidney. However, the most significant concerns regarding chronic exposure to low concentrations of methylmercury in fish are for neurological effects in the developing fetus and children.

Recently, the U.S. Environmental Protection Agency (EPA) issued a national advisory concerning risks to children and to pregnant or nursing women associated with mercury in freshwater fish caught by their friends and family (EPA 2001). The groups most vulnerable to the effects of mercury toxicity include: women who are pregnant or may become pregnant, nursing mothers, and young children. To protect against the risks of mercury in fish caught in freshwater, EPA has recommended that these groups limit fish consumption to one meal per week for adults (6 ounces of cooked fish, 8 ounces of uncooked fish) and one meal per week for young children (2 ounces of cooked fish or 3 ounces of uncooked fish). The National Academy of Sciences confirms that methylmercury is a potent toxin and concludes that the babies of women who consume large amounts of fish when pregnant are at greater risk for changes in their nervous system that can affect their ability to learn (NAS 2000). The advice from EPA was issued to raise awareness of the potential harm that high levels of methylmercury in fish can cause to child's developing brain and nervous system. This advice provides guidance on the amount of fish caught by friends and family that these groups can eat to keep methylmercury from reaching harmful levels.

1.6 Phased Approach to the TMDL

In a phased TMDL, EPA or the state uses the best information available at the time to establish the TMDL at levels necessary to implement applicable water quality standards and to make the allocations to the pollution sources where applicable. However, the phased TMDL approach recognizes that it may be necessary to collect additional data and information to validate the assumptions of the TMDL and to provide greater certainty that the TMDL will achieve the applicable water quality standard. In the case of the TMDL for mercury in McPhee and Narraguinnep Reservoirs, Phase 1 consists of the following: identification of data and information to be collected, data collection, modeling of the results, and load allocation estimates. This information has been summarized in two documents:

1. Tetra Tech. 2000. Review of Past and 1999 Mercury Data and Related Information for six Colorado Reservoirs.

2. Tetra Tech 2001. Technical Support for Developing a Total Maximum Daily Load for Mercury in McPhee and Narraguinnep Reservoirs, Colorado.

These documents will form the basis of Phase 2 of the TMDL. In Phase 2, we intend to gather new information and perform new analyses so as to produce a revised TMDL for mercury in the identified Reservoirs. The phased approach is appropriate for this TMDL because numerous data gaps were identified in the Technical Support Document (summarized in Section 6, below) that formed the basis of Phase I (Tetra Tech 2001) and only rough estimates of actual contributions of mercury to McPhee and Narraguinnep Reservoirs from both point and nonpoint sources could be identified. Additional data collection, analysis, and modeling in Phase II will allow the state to better characterize load allocations in the future.

2. Applicable Water Quality Standards

TMDLs are developed to meet applicable water quality standards. These may include numeric water quality standards, narrative standards for the support of designated uses, and other associated indicators of support of beneficial uses. A numeric target identifies the specific goals or endpoints for the TMDL that equate to attainment of the water quality standard. The numeric target may be equivalent to a numeric water quality standard (where one exists), or it may represent a quantitative interpretation of a narrative standard. This section reviews the applicable water quality standards and identifies an appropriate numeric indicator and associated numeric target level for the calculation of the mercury TMDL for McPhee Reservoir and Narraguinnep Reservoir.

2.1 Numeric Water Quality

The designated use classifications of McPhee Reservoir are: Aquatic Life Cold 1, Recreation 1, Water Supply, and Agriculture. The designated use classifications of Narraguinnep Reservoir are Aquatic Life Warm 2, Recreation 2, and Agriculture. Colorado has adopted water quality standards for mercury that apply to these designated uses, specifying a Final Residue Value (FRV) criterion of 0.01 µg/L total mercury (CDPHE Water Quality Control Commission, Regulation No. 34). The mercury criterion is not hardness-dependent.

Colorado's numeric criterion for mercury in water is intended to ensure protection of the general population from potential adverse health impacts from the ingestion of sort-caught fish. The applicable criterion is the most restrictive of values derived for the protection of aquatic life, fish tissue concentrations, and drinking water supplies. It is based on based on a water quality value for total mercury that, through the process of bioaccumulation, will result in a Final Residue Value in fish tissue at the FDA action level of 1 ppm. Footnote 6 to Table III in CDPHE Regulation 31 (effective October 30, 2001, pp. 55-56) provides the following discussion relative to this criterion:

> "FRV means Final Residue Value and should be expressed as "Total" because many forms of mercury are readily converted to toxic forms under natural conditions. The FRV value of 0.01 µg/liter is the maximum allowed concentration of total mercury in the water that will present bioconcentration or bioaccumulation of methylmercury in edible fish tissue at the U.S. Food and Drug Administration's (FDA) action level of 1 ppm. The FDA action level is intended to protect the average consumer of commercial fish; it is not stratified for sensitive populations who may regularly eat fish.
>
> A 1990 health risk assessment conducted by the Colorado Department of Public Health and Environment indicates that when sensitive subpopulations are considered, methylmercury levels in sport-caught fish as much as one-fifth lower (0.2 ppm) than the FDA level may pose a health risk."

To date, mercury concentrations in water in McPhee and Narraguinnep Reservoirs have not exceeded the applicable water quality standards and the Reservoirs are listed as not supporting designated uses based on the presence of a fish consumption advisory, rather than excursions of ambient water quality standards for mercury.

2.2 Narrative Standards

Colorado's narrative language for toxics is expressed in part as follows (CDPHE Water Quality Control Commission, Regulation No. 31, effective October 30, 2001, Section 31.11:

> "Except where authorized...state surface waters shall be free from substances attributable to human-caused point source or nonpoint source discharges in amounts, concentrations, or combinations which:
>
> (a) for all surface waters except wetlands:
>
> (iv) are harmful to the beneficial uses or toxic to humans, animals, plants, or aquatic life..."

This clause may be taken to generally prohibit loading of mercury to the lake in amounts that result in fish tissue contamination levels sufficient to impair recreational uses or present a risk to human health.

2.3 Fish Consumption Guidelines

As noted above, McPhee and Narraguinnep Reservoirs are listed as not supporting the designated uses based on the presence of a fish consumption advisory, rather than excursions of ambient water quality standards for mercury. Both Reservoirs have been included on previous iterations of the 303d list, including those promulgated in 1993, 1994, and 1996. EPA guidance available in 1992 recommended that water bodies for which fish consumption advisories had been issued be included on the 303d list. EPA's recommendation is based on the Clean Water Act mandate that waters of the U.S. be: "fishable and swimable". EPA interpreted presence of a fish consumption advisory to be evidence of non-attainment of the "fishable" standard set forth in the statute.

Colorado does not have a formal regulation establishing a guideline for the issuance of fish consumption advisories due to the presence of mercury in fish tissue. However, CDPHE has issued fish consumption advisories for waterbodies where concentrations of mercury in fish fillets are equal to or exceed the action level of 0.5 mg/kg (wet weight) total mercury. CDPHE listings are based on the risk analysis presented in the May 6, 1991 Disease Control and Epidemiology Division *Position Paper for Draft Colorado Health Advisory for Consumption of fish Contaminated with Methylmercury*. This paper is presented in Appendix A. The risk assessment approach outlined in the paper is based on a toxicity value reference dose (RfD) of 0.3 µg/kg/day (EPA 1990) for non-pregnant adults and 0.075 µg/kg/day for women who are pregnant, nursing, or planning to become pregnant, and children nine years old and younger.

The following equation is used to determine recommended fish consumption rates for the two groups:

$$\text{Meals per Month} = \frac{RfD \times BW \times CF}{C \times IR}$$

where:

RfD = EPA Reference Dose, 0.3 μg/kg/day, adults; 0.075 μg/kg/day, women who are pregnant, nursing, or planning to become pregnant, and children nine years old and younger [10]

BW = Body weight, 70 kg [9];

CF = Conversion Factors of 7 days per week, and 4.35 weeks per month;

C = Concentration of mercury in edible fish tissue (wet weight analysis);

IR = Ingestion Rate: 227 g/meal for a 70-kg adult [6].

The table below compares recommended consumption levels for these two groups.

Consumption of Mercury Contaminated Fish

Concentration of mercury in edible fish tissue	Meals per month Children up to 9 years	Women who are pregnant, nursing, or planning to become pregnant
0.2 ppm[a,b]	7	3.5
>0.2 – 0.35 ppm	4	2
>0.35 – 0.7 ppm	2	1
>0.7 – 1.4 ppm	1	0
>1.4 – 2.8 ppm	0	0
2.8 ppm or more	0	0

[a] Parts per million (ppm) wet weight.
[b] A threshold effect level for methylmercury has not been observed. Therefore, young children and women who are pregnant, nursing or planning to become pregnant may wish to limit their consumption of fish with mercury concentrations below this level.

Based on the equation and the information in the table, a fish tissue concentration of 0.5 mg/kg was established as the approximate center of the range at which the safe consumption level is four meals per month for non-pregnant adults and one meal per month for women who are pregnant, nursing, or planning to become pregnant; and children 9 years of age or younger. This level was consistent with fish consumption advisory thresholds adopted by other states in the early 1990s.

It is important to note that on January 8, 2001, EPA posted a notice on a new 304(a) water quality criterion for methylmercury for the protection of human health in the Federal Register (Volume 66, Number 51). In it, they recommend that states adopt a fish tissue reside criterion of 0.3 mg methylmercury/kg fish into their water quality standards. The 0.3 mg/kg level is derived from a RfD of 0.1 μg/kg/day. Colorado is in the process of reviewing their fish consumption advisory policy based on this new information.

2.4 Selected Numeric Target for Completing the TMDL

The applicable numeric targets for the McPhee and Narraguinnep TMDLs are the Colorado water quality standard of 0.01 μg/L total mercury in the water column and the Fish Consumption Advisory action level of 0.5 mg/kg total mercury concentration in fish tissue. Water column mercury concentrations have not been found in excess of the ambient water quality standard; however, tissue concentrations have exceeded the action level. Fish in McPhee and Narraguinnep Reservoirs accumulate unacceptable tissue concentrations of mercury even though the ambient water quality standard appears to be met. The most binding regulatory criterion is the fish tissue concentration action level of 0.5 mg/kg total mercury, which is selected as the primary numeric target for calculating this TMDL.

Mercury bioaccumulates in the food chain. Within a lake fish community, top predators usually have higher mercury concentrations than forage fish, and tissue concentrations generally increase with age class. Top predators (such as bass) are often target species for sport fishermen. Risks to human health from the consumption of mercury-contaminated fish are based on long-term, cumulative effects, rather than concentrations in individual fish. Therefore, the criterion should not be applied to the extreme case of the most-contaminated age class of fish within a target species; instead, the criterion is most applicable to concentrations in a top predator species representing an average within the size class allowed to be caught and kept.

Within McPhee Reservoir, the top predator sport fish is the largemouth bass (*Micropterus salmoides*), which exhibits the highest mercury concentrations; however, creel surveys conducted in 1993 indicate that largemouth bass constitute less than 1 percent of the total catch. The top predator among sport fish regularly taken in McPhee is the smallmouth bass (*Micropterus dolomieui*; 19 percent of total catch in 1993). The lake water quality model is capable of predicting mercury concentrations in fish tissue for each age class at each trophic level. Average mercury concentrations in fish tissue of target species are assumed to be approximated by average concentration in 15-inch smallmouth bass. While this is the minimum keepable size for bass, and mercury body burdens are likely to continue to increase with increased length/age, it appears that few smallmouth bass in excess of 15 inches are present or caught in McPhee. Use of the 15-inch smallmouth bass thus provides a reasonable maximum estimate for long-term exposure of the fish-consuming public. **Therefore, the selected target for the TMDL analysis**

in McPhee Reservoir is an average tissue concentration in 15-inch smallmouth bass of 0.5 mg/kg or less.

In Narraguinnep Reservoir, the fish community differs from that in McPhee. Here the top predator sport fish, and also the fish with the highest reported tissue methylmercury body burden, is walleye (*Sitzostedion vitreum*). Walleye continue to bioaccumulate mercury with increasing size and age. The largest walleye analyzed in Narraguinnep are 18 inches in length. However, the sample size was small, and walleye in excess of 18 inches are likely to occur in the Reservoir. Until detailed creel surveys of Narraguinnep are conducted, it is not possible to exactly determine the age-size structure of the walleye population. **Therefore, the selected target for the TMDL analysis in Narraguinnep Reservoir is an average tissue concentration in 18-inch walleye of 0.5 mg/kg or less.** Because the water that supplies Narraguinnep is largely comprised of diversions from McPhee, the target established for Narraguinnep may also affect the TMDL calculations in McPhee.

3. Pollutant Source Assessment

There are a number of sources of mercury loading to McPhee and Narraguinnep Reservoirs, as described in Tetra Tech (2000). The sources external to the Reservoirs themselves may first be separated into direct atmospheric deposition onto the lakes (from both near- and far-field sources) and transport into the lakes from the watershed. For Narraguinnep, mercury in diversions from McPhee must also be considered. The watershed loading occurs in both dissolved and sediment-sorbed forms. Ultimate sources in the watershed include mercury in the parent rock, mercury residue from mine tailings and mine seeps, point source discharges, and atmospheric deposition on to the watershed, including deposition and storage in snowpack. Monitoring of streams and stream sediments typically reflects the combined impact of a number of these ultimate sources.

3.1 Point Sources

The EPA Permit Compliance System (PCS) identifies only two permitted discharges to water regulated under the NPDES system within the watersheds of McPhee Reservoir and none in the watershed of Narraguinnep Reservoir. The point sources in the McPhee watershed are the public sewer system for the town of Dolores (permit CO0040509) and a small private sewer system (Dolores River R.V.) located 2.5 miles east of Dolores (CO0042561).

The town of Dolores is located just upstream of the Reservoir on the Dolores River. A municipal sewage treatment plant and a series of municipal sewage treatment ponds are located in the southern end of the town adjacent to the Dolores River. These ponds consist of two settling ponds, two aeration ponds, and four sand-filter ponds. The public system has a permitted flow of 0.47 MGD to the treatment ponds with underdrains to the Dolores River. Average flows are about one-half of permitted flows. The effluent from these ponds enters the Dolores River upstream of the Reservoir via the underdrains, but these ponds can be flooded under extreme high water conditions.

The Dolores River R.V. system has a permitted average flow of only 0.012 MGD with weir discharge to the Dolores River.

Neither facility has permit limits for mercury. Given the small amount of flow, most of which does not discharge via direct surface pathways, point sources are not expected to provide a significant amount of mercury loading to the Reservoirs.

3.2 Mercury Sources from Mining Activities

Past mining activities are an important source of mercury load in the McPhee/Narraguinnep watershed. Mining activities can increase watershed mercury load in several distinct ways. First, mercury is present in many of the sulfide mineral ores of the watershed, and mine tailing piles can leach mercury and other metals. In addition, seeps from old mines can transport dissolved mercury to streams. Finally, in the past mercury was often directly in the gold mining process: before the introduction of cyanidation technology at the beginning of the 20th century, mercury amalgamation of precious metal ores was common practice throughout the western United States. This was often done through a ball mill process, in which the raw ore was crushed to a talc consistency and placed into a settling trough with water and elemental mercury. The gold amalgamated with the mercury and settled out. The excess water and overburden were washed out of the trough onto the ground, and the amalgam was collected and placed in a furnace, where the mercury was evaporated off, re-condensed into a retort, and saved for reuse. Some loss of mercury occurred in many steps in this metallurgical process. Most of the gold-mercury amalgam settled out and was recovered, but some was inevitably washed out of the trough with the fine overburden. The amalgam furnaces could also elevate local soil concentrations through short-range atmospheric deposition.

There are three large mining districts in the Dolores River watershed: the La Plata, the Rico, and the area around Dunton on the West Dolores River. The known mines in the vicinity of the Dolores River watershed are shown in Figure 3-1 and are listed in Appendix A of Tetra Tech (2000). Dolores County was a highly productive mining area for metals, primarily silver, gold, lead, zinc, and copper. In addition, there have been mines for coal, uranium, vanadium, magnesium, iron, sulfur, and sand and gravel. Five former coal mines were located in the Dolores River drainage, including one on Barlow Creek north of Rico, two on Lost Canyon Creek, one on upper Beaver Creek, and one on Haycamp Canyon, which enters the Dolores River close to the Reservoir.

The Upper Dolores River and the West Dolores River pass through several areas where gold and silver mining occurred beginning in the 1870s (Butler et al., 1995). Presently, there are no active gold or silver mines in the basin, but the historic mining has left an estimated 150 to 200 mine shafts, adios, and test pits in just the Rico area. An estimate of the land disturbed by former mining activity was 54 acres in the Rico and Dunton areas alone (CDNR, 1982). Mine drainage from these areas is a source of dissolved and suspended heavy metals, including mercury into the Dolores River.

La Plata Mining District

The La Plata district includes the upper parts of Bear Creek, a tributary to the Dolores River to the southeast of the Reservoir, and additional areas to the south. In the La Plata district, ore deposits were first discovered in 1873 (Eckel et al., 1949). Gold, silver, lead, and copper were mined. Four copper deposits occur along upper Bear Creek, a tributary to the Dolores River. Two large copper mines were located along Bear Creek: the Century mine in the upper Bear Creek watershed, and one at the mouth of the creek. Four mines, located on the upper reaches of Bear Creek, extracted both gold and copper, along with a copper mine at the mouth of the creek. The remaining mines of the La Plata district are to the south, outside of the Dolores River watershed. The minerals found in the La Plata ore deposits include cinnabar (HgS) and other sulfide minerals that can contain mercury. The La Plata ore deposits are unusual in that native mercury and coloradoite, a mercury telluride mineral, are present along with native gold and an amalgam of native gold, silver, and mercury (Eckel et al., 1949). Native mercury was noted to have been widespread in the near-surface workings of the earliest mines where supergene deposits were found, such as the Iridos mine and Ashland mine, which were located on tributaries to Junction Creek that eventually drains to the San Juan River, not the Dolores River. Finely divided free gold associated with pyrite was also obtained from the Century mine on the upper reaches of Bear Creek (Eckel et al., 1949). In many cases the native gold was associated with the tellurides of gold, silver, and mercury. Placer deposits of gold were present in some parts of the La Plata district and are of particular interest, as the mercury amalgamation process may have been used in the 1930s or earlier to obtain gold from the placer deposits along the creeks. Hobbyists have also used mercury to obtain gold from placer deposits.

Rico Mining District

The Rico mining district is on the Upper Dolores River and tributaries above the town of Rico near the confluence of Silver Creek and the Dolores River, about 30 miles upstream of McPhee Reservoir, as shown in Figure 3-1. See also the detailed inset in Figure 3-8 below. The primary ore of the Rico district was sulfide replacement deposits and contact metamorphic zones in the Hermosa Formation (McKnight, 1974), and some of these sulfide minerals contain mercury.

The Rico area has an extended mining history of which a detailed account can be found in URS (1994). Early mining activity in the Rico area began in the 1860s when several claims were staked in the Pioneer District at the confluence of Silver Creek with the Dolores River. Extensive mining took place in the 1870s for silver, lead, zinc, gold, and copper (McKnight, 1974). The mines were especially concentrated in the area between Deadwood Creek, Horse Creek, and Silver Creek. The latter two waterbodies were found to have mine tailings in their creek beds (E&E, 1991).

Silver production reached a peak in 1893. In 1902, all of the important mines in the district were consolidated under the United Rico Mine Company which primarily produced base metal ores. The Rico-Argentine Mining Company, was formed in 1915 to produce base metal ores. A custom mill was built in 1926 by the International Smelting Company, a subsidiary of Anaconda Mining Company. Base metal ore production peaked in 1927, but by 1928 the mill had shut down, and by 1932 all mining activity in the area had ceased.

The Rico-Argentine Mining Company resumed sporadic mining activities in 1934 and resumed steady production in 1939. A sulfuric acid plant located north of the settling ponds along the Dolores River was operated between 1955 and 1964. Operations consisted of a mill and tailings pond on Silver Creek and an acid plant, cyanide heap leach, and settling ponds on the Dolores River. There were two discharge points associated with the operation. Discharge point 001 was thedischarge from the Blaine Tunnel on Silver Creek. There is no longer discharge from 001 because it is redirected underground to the St. Louis Tunnel where it drains into the St. Louis Settling Pond System on the Dolores River. The outfall of the final pond into the Dolores River isdischarge point 002.

All mining operations again ceased in 1971 and most of the mine workings were allowed to flood and drain through the St. Louis Tunnel. The waste materials from the acid plant and drainage from the St. Louis Mine were flumed to tailings ponds adjacent to Silver Creek and the Dolores River, as shown in Tetra Tech (2000). These tailings ponds were poorly maintained and frequently ruptured during the winter (CDOW, 1973). For example, during the winter of 1966-1967, almost continual spillage of tailings into Silver Creek and the Dolores River were observed. These spills completely covered the bottom with gray deposits and orange-red iron oxide flocculent. This led to the loss of populations of aquatic organisms inhabiting Silver Creek and the downstream sections of the Dolores River (CDOW, 1973).

The Rico-Argentine Mining Company built a 300' by 500' leach pad next to the old sulfuric acid plant in 1973. A cyanide solution was used to leach silver and gold from raw ore, and an overflow of an unknown quantity of leaching liquour to the Dolores River occurred sometime in 1974. In 1975 an additional cyanide leach pad was constructed in a settling pond originally used by the acid plant.

An NOV and a Cease and Desist Order was issued to the Rico-Argentine Mining Company in 1990 by CDPHE because of the company's failure to meet compliance with its NPDES permit.

Anaconda purchased the property in 1980 and in response to the outstanding NOV and CDO, carried out several environmental efforts such as building a water treatment plant at the St. Louis Tunnel, capping wells, plugging adits, and stabilizing tailings and treatment ponds.

Rico Development Corporation purchased the property in 1988. NOVs and CDOs were issued to Rico Development Corporation in 1990 for violations of the NPDES permitted discharge levels of lead and silver standards, and in 1994 for violations of silver, lead and zinc standard.

The Atlantic Richfield Corporation (ARCO) (owner of Anaconda) initiated a voluntary environmental sites characterization of the town of Rico and surrounding area within the framework of the Colorado Voluntary Cleanup and Redevelopment Act (Analytical Results Report, Rico Argentine, Rico, Dolores County, Colorado TDD#9511-0015, 6/19/96).

The Rico-Argentine Mine is a CERCLIS Hazardous Waste Site (EPA ID CO980952519) subject to removal actions under the Superfund law. As of 2000, the Rico Development Corporation had dissolved. Ownership of the abandoned mine site is currently in dispute, resulting in a lack of maintenance of the tailing ponds designed to capture discharges from the Blaine Tunnel and St. Louis Tunnel (Mimiaga, 2000). In April 2000 EPA Region 8 undertook an emergency removal action to stabilize the pond embankments and prevent a catastrophic release of mine effluent into Silver Creek.

Five different gold and silver deposits, two gold deposits, and one silver deposit were shown in the Rico area on a list of major historic US Bureau of Mines deposits of gold and silver in Colorado from 1964 (Tetra Tech, 2000). A total of 10 large inactive metal mines were included from the Rico area on a 1982 Inactive Mine Inventory of Colorado prepared to help develop the Colorado Inactive Mine Reclamation Plan for the state (Bucknam, 1982). Other large mines in the Rico area include the Puzzle Mine on Horse Creek, the Poor Boy Mine, and Sambo Mine below Silver Creek; and the Iron Clad, Columbia, and Blue Bell Mines south of Rico. Active mine drains to the Dolores River are also present above Rico, including one mine drain on the mainstem of the Dolores and one mine drain upstream on Barlow Creek.

Several studies conducted by the Colorado Department of Game, Fish, and Parks during the 1960s found no fish or aquatic insects inhabiting the Dolores River below the Rico-Argentine min acid plant but thriving populations of fish and aquatic insects in the reach above the acid plant. There are still several large tailings piles located on the banks of Silver Creek along its lower reaches. The lower reaches of Silver creek also receive runoff from active acid mine seeps. This mining activity has dramatically affected present-day Silver Creek. There are still orange and red iron-stained areas on the rocks along the banks of the lower creek, and there is a lack of benthic invertebrates in the lower reaches of Silver Creek. Water and sediment sampling in the Rico area was conducted for the US EPA in 1985. Mercury was detected in sediment samples in the Rico area from both Silver Creek and the upper Dolores River at 0.1 to 0.12 mg/kg) (Morrison Knudsen, 1994). A sample from the tailings pond next to Silver Creek had 13 mg/kg, which suggests the presence of mercury sulfides such as cinnabar. Mercury was also higher in sediment below the Rico-Argentine Mine (0.54 mg/kg) than sediment from the Dolores River below Silver Creek (ND to 0.06 mg/kg) (Morrison Knudsen, 1994). Follow-up sampling on Silver Creek was conducted in September 1995 for the USEPA. Three water and sediment samples from Silver Creek had no detected mercury; the detection limit for water was 0.2 µg/L and 0.12 to 0.13 mg/kg for sediment (URS, 1996).

1999 sampling conducted by Tetra Tech included several samples of mine seeps and streams in the Rico area (see Section 3.5).

West Dolores / Dunton Mining Area

On the West Dolores River, mining activity for gold, silver, and copper was primarily located in the upper reaches above Cold Creek near Dunton, located about 36 miles upstream of the Reservoir. Large mines included Emma, Johnny Bull, Teaser, Privateer, and Little Silver. In addition to the mines, hot springs are present near the West Dolores River area, notably at Geyser's Hot Springs and Dunton. Mercury is often present in areas with hot springs, either in the water or as cinnabar (HgS) deposits (Saupe, 1972; Colorado Geological Survey, 1979). Four geothermal areas are also present in the Rico area (CGS, 1979). The larger geothermal areas are shown on the mines map (See Figure 3-1).

Natural gas wells are also located throughout the area of the McPhee Reservoir watershed. The closest gas wells to the Reservoir are located in the southeast area near House Creek. Mercury can be introduced from natural gas operations via spills from equipment containing mercury or from gas leaks where naturally occurring mercury is present in the gas itself. Mercury spills from pressure and density gauges are more common in deep wells over 400 ft deep. At present, there are no active drilling operations near the Reservoir; it is mostly gas pumping and distribution operations.

In general, the quantity of mercury loading from mining operations has not been measured directly. Instead, the loads must be estimated through combination of observed data in the water column and sediment (Section 3.5), coupled with the watershed linkage analysis (Section 4.4).

3.3 Atmospheric Deposition

Atmospheric deposition is an important source of inorganic mercury loading to surface waters. Much of this mercury is from a variety of anthropogenic sources. Atmospheric deposition can be divided into short-range or near-field deposition, which includes deposition from sources located near the watershed, and long-range or far-field deposition, which includes mercury deposition from regional and global sources. No direct measurements of atmospheric deposition of mercury within or near the McPhee-Narraguinnep watersheds are available at this time, although some measurements have been made of mercury in snowpack in the McPhee watershed.

Near-Field Atmospheric Deposition

Significant atmospheric point sources of mercury often cause locally elevated areas of near-field atmospheric deposition downwind. Mercury emitted from man-made sources usually contains both gaseous elemental mercury (Hg(0)) and divalent mercury (Hg(II)). Hg(II) species, because of their solubility and their tendency to attach to particles, are redeposited relatively close to their source (probably within a few hundred miles), whereas Hg(0) remains in the atmosphere much longer, contributing to long-range transport.

The fact that there is relatively low precipitation in southwestern Colorado means that less mercury is likely to be deposited near the source than in more humid regions; i.e., Hg(II) forms of mercury probably have time to migrate farther from their source before being scavenged by precipitation or dry depositing as particle-attached mercury.

Significant potential point sources of airborne mercury include coal-fired power plants, waste incinerators, cement and lime kilns, smelters, pulp and paper mills, and chlor-alkali factories. As described in Tetra Tech (2000), there are two large coal-fired power plants in the Four Corners area within about 50 miles of the McPhee and Narraguinnep Reservoirs: (1) Arizona Public Service - Four Corners Station, which has a 2,040 MW capacity and (2) the Public Service Company of New Mexico - San Juan plant, which has a 1,500 MW capacity. Twelve other coal-fired power plants are located with a 200 mile radius of the center of Narraguinnep Reservoir. Together, these plants generated nearly 81,405,000 MwH of electricity during 1998 (Pechan, 2001). There are also two gas-fired power plants in the Four Corners area and other gas-fired plants in the adjacent parts of Colorado and Utah, which would discharge less mercury than the coal-fired plants.

Because mercury is a volatile element, much of the mercury present in the coal is discharged via the stack to the atmosphere, unless technology is implemented to limit emissions. The discharged mercury may be in elemental, oxidized (ionic), or particulate form, with the mix depending on temperature and mercury reaction conditions, including chlorine and sulfur content (EPRI, 2000). In general, the oxidized and particulate forms of mercury are amenable to removal by control technology, while the elemental forms are not.

A rough estimate of the emissions of mercury from coal-fired power plants without advanced emission controls is about 70 percent of the amount contained in the incoming coal (EPRI, 1999). Split sample analyses of mercury content of coal used for power production during the winter of 1999-2000 in the Four Corners area are reported by Ingersoll (2000). These range from about 0.04 μg/g at Navajo to 0.09 μg/g at Four Corners.

After July 1999, large power plants were required to estimate their mercury emissions and provide the data to the USEPA Toxic Release Inventory. Detailed mercury data for a large number of plants were collected during 1999 as part of EPA's Information Collection Rule. Mercury emissions estimates have recently been summarized on line (http://www.epa.gov/mercury/plant_set_state.pdf; accessed 3/1/01). Detailed estimates of emissions for 1999 by plant and boiler are contained in the draft National Emissions Inventory (RTI, 2001). These estimates include influent and stack effluent mercury load after accounting for reduction expected for a given control technology. There is considerable uncertainty in the estimated rate of removal, as shown by the summaries in EPRI (2000). The control technologies (combination of boiler type, fuel, and sulfate, NO_x, and particulate matter controls) are identified by a group number or "bin". An accompanying table (http://www.epa.gov/ttn/atw/combust/utiltox/control2.zip, accessed 7/17/01) summarizes the average mercury speciation among particulate mercury, oxidized mercury, and elemental mercury as reported by control bin for the ICR. These fractions can be applied to the total mercury emission estimates to obtain estimates of the reactive mercury (particulate plus oxidized mercury) generated by each source.

Mercury emissions for the 14 coal-fired power plants within 200 miles are presented in Table 3-1 based on the EPA estimates (RTI, 2001). These estimates differ somewhat from those presented in EPRI (2000), but are generally similar. Plant locations are shown in Figure 3-2. Total emissions from the 14 plants amount to 1,636 kg-Hg/yr, of which more than half (about 950 kg) are associated with the San Juan and Four Corners generating plants, the two large facilities that lie within 50 miles of Narraguinnep.

Table 3-1. Estimated Mercury Emissions from Coal-Fired Power Plants near McPhee and Narraguinnep Reservoirs

Plant	Location	ORISPL	Distance to Narraguinnep (miles)	Bearing from Narraguinnep	Power Generation (MwH)[1]	Emission Control Type[2]	Total Hg Emissions (kg/yr)[3]	Reactive Hg Emissions (kg/yr)[3]
San Juan	Waterflow, NM	2451	39	S	11,618,217	20	472.5	35.4
Nucla	Nucla, CO	527	42	N	586,448	40	9.1	0.3
Four Corners	Fruitland, NM	2442	44	S	14,617,015	16/19	477.0	21.0
Cameo	Palisade, CO	468	92	NNE	517,354	7	0.9	0.6
Escalante	Prewitt, NM	87	118	S	1.362138	19	39.4	1.3
Hunter	Castle Dale, UT	6165	138	NW	9,053,611	10/12	37.5	3.7
Navajo	Page, AZ	4941	139	WSW	16,484,808	11	137.7	8.7
Sunnyside	Sunnyside, UT	50951	142	NW	379,592	27	0.05	0.02
Bonanza	Vernal, UT	7790	144	N	3,458,586	12	1.4	0.6
Huntington	Huntington, UT	8069	158	NW	6,452,895	10/1	67.4	39.5
Carbon	Helper, UT	3644	163	NW	1,288,602	1	18.0	13.4
Cholla	Joseph City, AZ	113	165	SSW	6,370,902	16/14/20	116.1	9.0
Coronado	St. Johns, AZ	6177	165	S	4,797,610	20	113.4	4.8
Springerville	Springerville, AZ	8223	178	S	5,779,231	18	145.9	7.8
TOTAL					**81,404,873**		**1,636.4**	**146.0**

Notes to Table 3-1:

1. 1998 generation from E-GRID2000PC database (Pechan, 2001).
2. Emission Controls from National Emissions Database (RTI, 2001):
3. 1999 emission estimates from National Emissions Database (RTI, 2001). Reactive mercury estimates determined from application of speciation data in BinTable.xls (http://www.epa.gov/ttn/atw/combust/utiltox/control2.zip, accessed 7/17/01). Data from individual plants used where reported; otherwise calculated from national average speciation by control type.

Group	Primary Fuel	Boiler/Furnace	PM Control	SO_2 Control	External NO_x Control
1	Bituminous	CONV/PC	ESP-CS	None	None
5	Bituminous	CONV/PC	PARTSCRUB	None	None
7	Bituminous	CONV/PC	BAGHOUSE	None	None
10	Bituminous	CONV/PC	ESP-CS	WETSCRUB	None
11	Bituminous	CONV/PC	ESP-HS	WETSCRUB	None
12	Bituminous	CONV/PC	BAGHOUSE	WETSCRUB	None
14	Subbituminous	CONV/PC	ESP-HS	None	None
16	Subbituminous	CONV/PC	PARTSCRUB	None	None
18	Subbituminous	CONV/PC	BAGHOUSE	SDA	None
19	Subbituminous	CONV/PC	ESP-CS	WETSCRUB	None
20	Subbituminous	CONV/PC	ESP-HS	UB	None
27	Waste Bituminous	FBC	BAGHOUSE	None	None
40	Subbituminous	FBC	BAGHOUSE	None	SNCR

The plants in the Four Corners area believed to be, under average conditions, upwind of McPhee and Narraguinnep Reservoirs, as the prevailing wind direction in this part of Colorado is generally from the southwest (E&E, 1991). There are no first-order meteorological stations in this part of Colorado to confirm wind directions at McPhee and Narraguinnep. Further, wind patterns in this region are expected to be complex due to the terrain. Wind rose analysis at the Gallup, NM weather station does show a southwesterly pattern, with the direction of wind origin falling between the south and west about 40 percent of the time. Hourly surface wind data is also collected at the Mesa Verde National Park, Colorado CASTNET (EPA Clean Air Status and Trends Network) station, located south of McPhee Reservoir toward Four Corners. Surface winds at this station are predominantly from the NNW, likely reflecting local topographic control. Given the topography of the area, it would probably be necessary to undertake a modeling analysis on a set of continuous grid-based wind field estimates (such as that provide in NOAA's Eta Data Assimilation System [EDAS]) to derive an accurate evaluation of regional patterns of atmospheric transport.

While the regional emissions of mercury from coal-fired power plants are large, Table 3-1 also shows that these emissions are primarily in the form of elemental mercury. (The venturi scrubber technology used at a number of the plants generally has relatively low total mercury removal efficiency, but results in predominantly elemental mercury in the exhaust gas [EPRI, 2000].) Based on the ICR speciation data, the total emissions of reactive mercury from these plants amounts to 146 kg/yr, or 9 percent of the total emissions. The estimated reactive fraction varies widely by boiler from 3.4 percent at plants using subbituminous coal with wet scrubbers for SO_2 control to 74 percent for plants using bituminous coal with no SO_2 controls. The large plants near the Reservoirs to the south (Four Corners and San Juan) both have SO_2 controls that apparently eliminate a large fraction of the reactive mercury. The only plants in the area with large (>50 %) fractions of reactive mercury in their emissions are Cameo, Huntington Unit 2 and Carbon (Units 1 and 2), all located to the north of the Reservoirs. Figures 3-3a and 3-3b show the relative magnitude of total and reactive mercury emissions from the plants. The Four Corners and San Juan plants are important emitters of reactive mercury only because of their large size. Huntington, on the other hand, appears to emit a disproportionately large share of reactive mercury due to its lack of SO_2 controls.

As far as can be determined by the authors, no long-term regional modeling of atmospheric deposition has been completed for southwestern Colorado. An AIRMoN deposition site was operated in Waterfall Canyon near Telluride, CO, at an elevation of 3,200 meters just north of the McPhee watershed, during the summer of 2000, with the intention of investigating atmospheric deposition of nitrogen in the San Miguel River basin (Williams, 2001). AIRMoN sites differ from NADP deposition sites in collecting data at a short time scale (event basis), versus the weekly totals reported by NADP sites. This increased temporal resolution allows evaluation of potential sources of deposition during individual events.

Williams (2001) reported that nitrogen deposition rates at the AIRMoN site were between 25 and 50 percent higher than deposition rates at the nearby NADP sites at Molas Pass and Wolf Creek pass, and suggested that "the San Juan Mountains as a whole appear to be at risk to atmospheric deposition of inorganic nitrogen." Williams used the HYSPLIT-4 model to conduct back trajectory and forward trajectory analyses of air masses during five high-deposition events, and noted that "air masses with large amounts of inorganic nitrogen in wetfall...passed over or near coal-fired plants. Coal-fired power plants thus appear to be the primary source of elevated amounts of inorganic nitrogen in wetfall to the San Juan Mountains..." This conclusion was also supported by principal component analysis of common ions in wetfall. Of the five deposition events modeled, three derived from the west (generally tracking over Utah power plants), and two from the south (generally tracking over the Four Corners area). Williams also "suggests a strong possibility that there are elevated levels of mercury deposition to high-elevation areas of the San Juan Mountains", although mercury data were not collected at the AIRMoN site.

The preliminary results reported by Williams (2001) are intriguing, as they suggest that elevated atmospheric deposition of power plant emissions may occur on the southwest face of the San Juan Mountains. Although suggestive, the work does not identify specific sources of deposition, nor does it discern the relative contribution of near or distant sources.

In sum, power plants within a 200-mile radius of Narraguinnep Reservoir emit a relatively large total mercury load, which is likely to be transported toward McPhee and Narraguinnep, but the reactive mercury component of this load is relatively small. Do these loads constitute a significant source of mercury loading the Reservoirs? It is not fully possible to answer this question at this time. First, there is no monitoring of atmospheric mercury deposition available for southwestern Colorado. Second, no modeling of atmospheric transport and deposition from any of the coal-fired plants in this region has been undertaken. It appears clear that the mercury emitted from these plants provides some contribution to the mercury loading to the surface of McPhee and Narraguinnep Reservoirs; however, the significance of this loading cannot be assessed at this time. Accordingly, the analysis presented in this document proceeds with a generalized estimate of atmospheric deposition rates, without attribution to specific sources.

Estimates of mercury deposition rates at the Reservoirs are presented below. Applying simple screening procedures for air transport (USEPA, 1992), it does not appear that the reactive mercury emissions from nearby plants are sufficient to account for the estimated mercury deposition rates at the Reservoirs, by orders of magnitude. In general, significant large-scale impacts of local reactive mercury emissions are expected to occur within 10 km or so of the source, whereas the nearest major source to these lakes is over 40 miles away.

Instead, mercury deposition at the Reservoirs is more likely affected by oxidation and deposition of elemental mercury, as discussed further below. Elemental mercury can be transported over long distances in the atmosphere, and the pool of elemental mercury available for conversion to reactive form and deposition in southwestern Colorado likely derives from the net loading of distant and nearby sources. The nearby power plants likely contribute to atmospheric deposition loads at McPhee and Narraguinnep Reservoirs by increasing the available pool of elemental mercury. The extent of this contribution, however, has not been established at this time and must await further investigation, including the establishment of a mercury deposition monitoring site in the area.

The USEPA AIRS database was also searched to identify nearby incinerators for refuse, medical waste, or cement kilns (Tetra Tech, 2000). There were no incinerators within 50 miles of

McPhee or Narraguinnep Reservoirs. The nearest one was a cement kiln in Ridgway on the eastern slope of the San Juan Mountains; there were three other facilities further north.

Mercury mobilization and redeposition from soils during forest fires could also play a significant role in this fire-prone region, but is not well understood at this time.

Long-Range Atmospheric Deposition

Long-range atmospheric deposition (regional atmospheric background) is a major source of mercury in many parts of the country. The long-range component is driven in large part by the transport of elemental mercury. Because of its high volatility, deposition rates of elemental mercury are low. Significant deposition occurs when elemental mercury is converted to ionic forms. Elemental mercury derived from both long-range and nearer sources determines the local concentration of elemental mercury that is available for ionization and deposition.

In a study of trace metals contamination of reservoirs in New Mexico, it was found that perhaps 80 percent of mercury found in surface waters was coming from long-range atmospheric deposition (Popp et al., 1996). In other remote areas (e.g., Wisconsin, Sweden, and Canada), atmospheric deposition has been identified as the primary (or possibly only) contributor of mercury to waterbodies (Watras et al., 1994; Burke et al., 1995; Keeler et al., 1994).

Glass et al. (1991) reported that mercury released from sources up to 2500 km distant contributed to mercury levels in rain water deposited on remote sites in northern Minnesota. Studies of mercury contamination of soil have been correlated with regional-scale transport and deposition, with an increasing mercury gradient from west to east in the United States associated with the degree of regional industrialization (Nater and Grigal, 1992).

In the RELMAP modeling (USEPA, 1997, Section 5.1.3) comparisons are presented between wet deposition of mercury from local anthropogenic sources and a global-scale background concentration. While the RELMAP modeling is now believed to be outdated and does not fully reflect the current state of understanding of atmospheric chemistry leading to deposition of mercury (personal communication from O. Russell Bullock, USEPA, to J. B. Butcher, Tetra Tech, 7/25/01), these results suggested that the deposition of mercury in southwestern Colorado has a strong global or long-range component. The RELMAP model developers now suspect that the estimated rates of global atmospheric deposition presented for the Colorado area in USEPA (1997) may be too low. The broad-scale RELMAP modeling also could not take into account the effects of local topography on deposition, nor does it account for the interaction of chloride ions in power plant emissions with elemental mercury to form species such as mercuric chloride that are subject to more rapid deposition. EPA is now in the process of developing a new regional mercury transport model based on the Models-3/CMAQ system (Byun and Ching, 1999) and incorporating a more sophisticated representation of mercury chemistry. Preliminary results from the new model are not anticipated until 2002 (personal communication from O.R. Bullock, USEPA).

Deposition and Storage in Snowpack

A potential concern for the high-altitude watershed feeding McPhee Reservoir is atmospheric deposition of mercury, from both near-field and long-range sources, to the winter snowpack. Conceptually, mercury loading could be enhanced during snowmelt as this could release mercury load accumulated and stored over the winter. However, because elemental mercury is volatile and ionic mercury may leach through the snowpack, only a fraction of the deposited mercury may remain in the snowpack at spring melt.

To investigate these issues, USGS (Ingersoll, 2000) undertook snowpack sampling at the Lizard Head Pass SNOTEL site, at high elevation in a remote headwaters portion of the McPhee watershed, on February 26, 2000, prior to the start of snowmelt. In all three samples, mercury was non-detect at an 0.0003 μg/L (0.3 ng/L) concentration level. In contrast, total mercury concentrations in McPhee tributary streams in June 1999 ranged from 1 to 21 ng/L (Tetra Tech, 2000). These results suggest that snowpack storage of atmospheric mercury is not a significant factor in the overall mercury loading to the Reservoirs, at least for 1999.

Mercury Deposition Monitoring

Only limited monitoring of atmospheric deposition of mercury is available in the Southwest. Dry and wet deposition were measured in the Pecos River basin of eastern New Mexico in 1993-1994 (Popp et al., 1996). Average weekly deposition rates were calculated to be 140 ng/m^2-wk of mercury from dry deposition and 160 ng/m^2-wk of mercury from wet deposition. These data demonstrate the importance of both dry and wet deposition as sources of mercury.

The Mercury Deposition Network (MDN) measures wet deposition of mercury at a number of locations around the U.S. Operations began in February 1995 and have expanded in succeeding years. Stations are located mainly in the upper Midwest, Northeast, and Atlantic seaboard, with only a few in the west. Summaries of 1997 through 1999 MDN annual results (http://nadp.sws.uiuc.edu/mdn) show volume-weighted average concentrations of mercury in wet deposition varying from 3.8 ng/L to 23.0 ng/L for stations with greater than 75 percent data completeness. Average annual wet deposition rates for the same stations ranged from 3.9 μg/m^2 to 27.2 μg/m^2.

Only one MDN station is located in Colorado, and the only other MDN station in the southwest is in southern New Mexico (Figure 3-4). MDN monitoring records from these stations for 1998-2000 were obtained from the MDN web site and are provided in Appendix B.

The Colorado station is at Buffalo Pass (CO97), located in northern Colorado, and has been operational only since October 1998. During the complete monitoring years of 1999-2000, the volume-weighted mean volatile wet mercury deposition concentration at this station was 9.99 ng/L, and the wet deposition rate of total mercury extrapolated to a whole year basis was 11.99 μg/m^2/yr. The volume-weighted concentration estimate is calculated from the weekly data that are not flagged as invalid.

The station at Caballo, New Mexico (NM10) began collecting data in May 1997. Valid data for 1998-2000 show a volume-weighted mean mercury concentration of 21.5 ng/L and a wet deposition rate of 5.72 μg/m^2-yr. In 1998, Caballo had the highest volume-weighted concentration but lowest total wet deposition of all MDN stations with greater than 75 percent data completeness. The combination of higher concentration and lower total deposition at Caballo as compared to Buffalo Pass reflects the substantially lower rainfall at this station.

Atmospheric Loading Estimates

The mercury concentrations and deposition rates observed at Buffalo Pass and Caballo are unlikely to be the same as deposition rates to the McPhee and Narraguinnep watersheds. These stations are hundreds of miles distant from the McPhee/Narraguinnep area, and experience different meteorological patterns. Estimates from Buffalo Pass and Caballo will also not account for any influence of near-field sources on deposition at McPhee/Narraguinnep. On the other hand, the Buffalo Pass and Caballo data provide the only direct evidence on mercury deposition that is currently available for this region. A reasonable assumption is that the wet deposition volume-weighted mean concentration of mercury at McPhee and Narraguinnep Reservoirs is within the range represented by the moderate concentrations observed at Buffalo Pass (10 ng/L) and the high concentrations observed at Caballo (21.5 ng/L).

To further quantify the potential mercury deposition at McPhee and Narraguinnep Reservoirs, a surrogate approach was undertaken, in which the Buffalo Pass mercury deposition estimates are scaled by measures of atmospheric deposition of sulfate and nitrate.

Both sulfate and nitrate are key components of coal-fired power plant emissions, but may also arise from other sources. For instance, gas-fired sources emit large quantities of nitrate in southwestern Colorado (CDPHE, 1999). Our analysis of nitrate and sulfate deposition for western Colorado showed no readily apparent strong spatial patterns, once the influence of elevation is factored out. As a result, the estimated rates of mercury deposition at the Reservoirs also show an elevational effect, but not a geographic effect. Estimation of mercury deposition as proportional to sulfate and nitrate deposition is based on the assumption that wet and dry deposition of mercury is largely a function of scavenging of reactive gaseous mercury and therefore follows a process similar to the deposition of sulfate and nitrate. It is therefore a reasonable assumption that elevational effects similar to those observed for sulfate and nitrate concentrations should also apply to mercury. There do not appear to be currently any direct (monitoring) data that have been collected in North America or elsewhere that would clearly support or refute this hypothesis.

In sum, the approach taken to estimate atmospheric deposition of mercury is a first-order, scoping approach which is believed to approximate mercury deposition rates at the Reservoirs. It is not a substitute for actual measurements and detailed modeling of mercury deposition. EPA has proposed establishing an MDN station at Mesa Verde National Park, which will provide actual mercury deposition estimates in the neighborhood of McPhee and Narraguinnep Reservoirs.

The National Atmospheric Deposition Program (NADP, at http://nadp.sws.uiuc.edu/napata) maintains a relatively dense array of sites in Colorado, as shown in Figure 3-5. Data were obtained for seven active sites, mostly located in western Colorado (CO00, CO19, CO91, CO96, CO97, CO98, and CO99). CO97 is also the Buffalo Pass MDN station. For the analysis, sites CO00, CO91, CO96, and CO99 were selected due to proximity to McPhee and Narraguinnep

Reservoirs. CO97 was selected because it is the MDN station. In addition, CO97 is about 50 miles downwind of the power plant at Craig, CO, and thus is about the same distance from a coal-fired mercury source as are the Reservoirs. Sites CO19 and CO98 were selected both because they are in relatively close proximity to Buffalo Pass and because they represent sites with small lateral separation but significant elevation difference.

Records from these seven stations for 1990-1999 were used as surrogates to estimate general deposition rates of pollutants associated with coal-fired boilers in southwestern Colorado. The data used in the analysis were selected from weekly results flagged as valid in the NADP database with codes "w" or "wa". The number of valid weekly observations from 1990 to 1998 range from 246 at CO00 to 365 at CO98. Data prior to 1989 were not used because of the potential changes in sulfate and nitrate deposition occurring as a result of the 1990 Clean Air Act. Data after 1998 were not available in final form at the time the analysis was conducted

Sulfate and NO_3 deposition rates exhibit a significant elevation effect in the Rockies, with higher deposition at lower altitudes. This elevation effect must be taken into account in transferring results to other locations. In addition, there have been temporal changes, reflecting both emission reductions for individual plants with new control technology under Clean Air Act requirements (e.g., low NO_x burners) and increases associated with increased generation capacity. In western Colorado, the recent NADP data show a decreasing trend with time for SO_4 and an increasing trend with time for NO_3 deposition. The NADP data do not reveal a spatial gradient in Colorado that is not explained by elevation. In 1996, 1997, 1998, and 1999 sulfate and nitrate ion concentrations in deposition were higher at station CO99 (Mesa Verde National Park) in extreme southwestern Colorado than at other stations farther north and east. While CO99 is nearer to the Four Corners power plants than the other stations, the difference in concentration appears to be adequately explained by difference in elevation.

The following cross-sectional models were derived from the NADP data:

$$LN(SO_4) = 8.0934 - 1.1243 \cdot LN(Elevation) + 0.06237 \cdot LN(Year), \quad R^2 = 0.404$$
$$LN(SO_4) = 6.6828 - 0.9041 \cdot LN(Elevation) + 0.03764 \cdot LN(Year), \quad R^2 = 0.411$$

where SO_4 and NO_3 are volume-weighted means in mg/L and elevation is in meters.

Figures 3-6 and 3-7 show model predictions against observations of annual sulfate and nitrate deposition rates at the seven Colorado stations.

The equations for SO_4 and NO_3 were used to assess the relative impact at each Reservoir, with the assumption that higher wet SO_4 and NO_3 deposition would be closely correlated with higher wet mercury deposition.

The SO_4 and NO_3 data from 1990 to 1999 were used to develop the empirical models as a function of elevation and time. The ratios of Hg concentration in wet deposition to both SO_4 and NO_3 were calculated from the complete year 1999 data (only) and applied to 1995-1998 estimates of SO_4 and NO_3 deposition at each of the Reservoirs. The annual averages by each method were themselves averaged to estimate wet mercury deposition. While the fit of the sulfate and nitrate models differ, there is no a priori reason to suspect that one model is superior to the other in predicting mercury deposition. The results of the two models were therefore combined to provide a more robust estimate. The calculation was made using only the 1999 data because these data were all that were available at the time the lake model was constructed. Recalculation of the estimates with the 1999-2000 data would reduce the estimates by less than 5 percent.

Table 3-2 summarizes the resulting mercury wet deposition volume-weighted mean concentrations at the Reservoir surfaces. These estimates fall in the center of the range between the Caballo and Buffalo Pass volume-weighted mean concentrations, and thus appear reasonable. Estimated average annual precipitation, based on 1980-1999 data from the Dolores COOP station, converts the concentrations to an areal loading rate. Surface areas at full pool are used in this table to provide an upper bound and because direct deposition on the shoreline is likely to be easily washed into the Reservoir. Estimates were further partitioned by month based on the seasonal pattern of mercury deposition observed at Buffalo Pass. Both the volume-weighted mean concentration and the estimated wet deposition rate are well within the range of observations from other MDN stations.

Table 3-2. Mercury Wet Deposition Estimates for Colorado Reservoirs

	McPhee	Narraguinnep
Volume-weighted mean wet Hg concentration (ng/L)	16.0 (10-21)	16.8 (10-21)
Precipitation basis (in/yr, at Dolores, CO, 1980-1998)	20.7	20.7
Wet Hg deposition ($\mu g/m^2$-yr)	8.4 (5.2-11.0)	8.8 (5.2-11.0)
Surface area at full pool (acres)	4,470	625
Total wet Hg deposition (g/yr)	152 (95-200)	22 (13-28)

Note: Parentheses show range based on the observed volume-weighted mean concentration at Buffalo Pass (low) and Caballo (high) MDN stations.

The estimates in Table 3-2 include wet deposition only, as the MDN network does not measure dry deposition. Although there are few direct measurements to support well-characterized estimates and reliable sampling protocols have not been standardized, dry deposition of mercury often is assumed to be of the same order of magnitude as wet deposition (e.g., Lindberg et al., 1991). Dry and wet deposition were measured in the Pecos River basin of eastern New Mexico in 1993-1994 (Popp et al., 1996). Average weekly deposition rates were calculated to be 140 ng/m^2-wk of mercury from dry deposition and 160 ng/m^2-wk of mercury from wet deposition, but the dry component is likely higher in this area than in the McPhee watershed due to lower average annual rainfall. Throughfall studies in a coniferous forest indicate that dry deposition beneath a forest canopy could be on the order of 50 percent of the wet deposition signal (Lindqvist et al., 1991). These data demonstrate the importance of both dry and wet deposition as sources of mercury. Lacking direct evidence from Colorado, it was assumed that dry mercury deposition in these watersheds was, most likely, on the order of 65 percent of wet deposition, based on project team experience in other areas. This yields estimates of total direct mercury deposition shown in Table 3-3. A range is also shown, based on the range of wet deposition estimates shown in Table 3-2 and dry-to-wet ratios from 50 to 100 percent. While Narraguinnep receives much less total atmospheric deposition of mercury than McPhee, areal deposition rates are slightly higher, due to its smaller size.

Table 3-3. Total Atmospheric Mercury Deposition Estimates to Reservoir Surface

	McPhee	Narraguinnep
Total mercury deposition (g/yr)	251 (142-400)	37 (20-56)
Areal deposition rate (μg/m²/yr)	13.9	14.6

Note: Numbers in parentheses show range based on the range presented in Table 3-2 and dry-to-wet deposition rates varying from 50 to 100 percent.

The total mercury deposition rates estimated for McPhee and Narraguinnep are comparable to a recent deposition rate of 12.5 $\mu g/m^2/yr$ measured in sediment in Wisconsin and Minnesota lakes (Swain et al., 1992).

The estimated total mercury deposition rates may also be compared to the broad-scale deposition rates developed by USEPA (1997, Ch. 5), which suggested, for southwest Colorado, a regional background total mercury deposition rate on the order of 2 to 3 $\mu g/m^2/yr$. Estimated areal deposition rates for McPhee and Narraguinnep in Table 3-3 thus appear to be elevated relative to the broad-scale estimates for the area provided by RELMAP. The spatial resolution of RELMAP was not sufficient, however, to account for elevation effects, and the background deposition rates used in RELMAP for the western U.S. are suspected to be low. Deposition of mercury at McPhee and Narraguinnep could be elevated in part due to contributions from downwind coal-fired power plants and other anthropogenic sources. It should be reiterated, however, that (1) no local atmospheric monitoring has been conducted to confirm the estimates of mercury deposition rates to the Reservoirs, and (2) plume models of atmospheric transport of mercury from individual power plants have not been constructed.

Both the magnitude and source of the atmospheric mercury deposition to McPhee and Narraguinnep are subject to considerable uncertainty at this time. Uncertainty in atmospheric deposition estimates does not have a significant impact on the calibration of a lake mercury response model for McPhee Reservoir, because mercury loading to this lake is dominated by watershed sources. Uncertainty in atmospheric deposition may, however, have a significant impact on the estimation of load allocations to achieve water quality standards in Narraguinnep Reservoir, as is discussed further in Chapters 5 and 6.

Atmospheric deposition also contributes mercury to the watershed land surface. Elevated concentrations of mercury in the watershed and in the Reservoirs may in part be due to elevated historical atmospheric discharges. Further, changes in atmospheric deposition should ultimately result in changes in mercury concentration in soil available for washoff. The linkage is not a direct one, however, as mercury deposited on the land surface may revolatilize or become immobilized. Some evidence suggests that forest fires may play an important role in recyclying mercury from surface soils to the atmosphere. USEPA (1997, pp. 7-4) states: "Of the mercury deposited to watershed soils, a small fraction is ultimately transported to the waterbody. Deposition to and evasion from soils as well as the amount of reduction in upper soil layers are important factors in determining soil concentrations of mercury." There is not a good quantitative understanding of these processes at this time, and it is not possible to determine the net contribution of atmospheric sources to the land surface relative to geologic sources in mercury loading from the watershed. Atmospheric contributions to the watershed are therefore included within the estimates of nonpoint background load in Section 3.4.

3.4 Nonpoint Background Load

The Dolores River basin is located in the southeastern part of the Paradox basin. Geologic formations in the main Dolores River watershed include alluvium, underlain by intrusive igneous rocks forming dikes, sills, lacoliths, and stocks, above the Mancos shale and Dakota sandstone, and other shale, sandstone, and limestone formations (Whitfield et al., 1983). These formations are underlain by the Paradox salt member of the Hermosa Formation, which acts as a confining bed separating the groundwater into two systems. The salt formation has some shale, dolomite, and anhydrite layers, which can contain brine, oil, and natural gas. The natural gas is associated with the shale and dolomite formations beneath the salt anticlines that form confining units. Some oil has also been found in exploratory holes drilled beneath these salt formations. The formations beneath the salt beds include the Molas Formation of interbedded red siltstone, sandstone, limestone, and shale; the Leadville limestone; the Ouray and Elbert limestone and shale formations; and the Ignacio quartzite formation, overlying the Precambrian basement rocks of granite and other igneous and metamorphic rocks (Tetra Tech, 2000).

The intrusive igneous rocks, particularly the diorite monzonite and diorite-monzonite porphyry dikes, contain a variety of minerals that can contain mercury. The Rico Mountain Complex, where many of the heavy metal mines were located, consists of monzonite, and monzonite porphyry that was later hydrothermally altered, and intrusive monchiquite dikes. Similar intrusive dikes are also present in the Rio Lado Creek drainage, a tributary to the Dolores River south of Rico. In the Rico area, the dikes have intruded a sandstone and cherty limestone formation and a sandstone and shale unit of the Hermosa Formation (CDNR, 1982). The ores are found in faulted zones of these formations. The West Dolores River near Black Mesa also has sills and dikes of intrusive igneous rocks, chiefly calcic granodiorite, lamprophyre, and rhyolite, that may contribute elevated trace metals including mercury to this river (USBR, 1998). Faults are present in the House Creek area and the Geyser Springs area on the West Dolores River, which are sometimes associated with hot springs and intrusive formations. Mercury can also be associated with hot springs (CGS, 1979).

The soils in the watershed include red loam soils derived from the Dakota sandstone and gray alluvial soils derived from the Mancos shale and Mesaverde Formation of Cretaceous age. The average mercury of soils in southwestern Colorado is 0.5 to 1.3 mg/kg (Shacklette, 1984). In some areas, the B soil horizon can contain mercury at concentrations up to 4.6 mg/kg (Morrison-Knudsen, 1994b) and some sedimentary rock formations in the Colorado Plateau can contain up to 10 mg/kg (USGS, 1970). Shale can contain high concentrations of metals, as it is derived from clays, which adsorb metals. Thus, shale formations can be a source of mercury to runoff or streams.

Soils within the watershed also exchange mercury with the atmosphere, as noted above. Because the net balance of mercury deposition and volatilization at the land surface is not known, atmospheric deposition on the land surface is treated as part of the generalized watershed load (see Section 4.4).

3.5 Mercury Concentrations in Watershed Water and Sediment

Although loads from individual nonpoint sources within the watershed are difficult to measure directly, the cumulative impact of these sources can be examined through the mercury concentrations in water and sediment in the watershed. Initial investigations of mercury in the watershed were undertaken by USEPA in 1985 and by USGS and USBR in 1989 and 1992, as discussed in Tetra Tech (2000). Due to high detection limits and lack of ultra-clean sampling and analytical techniques, these data are of limited value for quantitative analysis. They do, however, suggest elevated levels of mercury loading from the Silver Creek sub-basin.

Additional extensive sampling in the watershed using ultra-clean techniques was undertaken in 1999. The mercury samples were taken during two separate monitoring events: the first over the period from June 4, 1999 to June 17, 1999 and the second from August 2, 1999 to August 7, 1999. The location of the monitoring sites in the McPhee/Narraguinnep watersheds are presented in Figure 3-8 and Table 3-4. Table 3-4 also provides total mercury results for water and sediment. A more detailed discussion of the sampling results, along with results for dissolved total mercury and total and dissolved methyl mercury, is provided in Tetra Tech (2000).

Table 3-4. Total Mercury Results from 1999 Sampling, McPhee and Narraguinnep Reservoir Watersheds

Sample ID	Location	Unfiltered Total Mercury in Water (ng/L)		Total Mercury in Sediment (ng/g dry weight)	
		June 1999	August 1999	June 1999	August 1999
MCP-1	Pond near Dolores Treatment Plant	3.65	1.10	9.56	47.54
MCP-2	Lost Canyon Creek	2.34	1.73	4.29	2.37
MCP-3	West Dolores River near Mouth	3.18	1.64	3.74	41.61
MCP-4	West Dolores River - Upper	5.62	1.57	13.78	29.75
MCP-5	Dolores River above W. Dolores River	3.98	1.58	13.70	41.19
MCP-6	Garrison Canyon	1.50		3.85	7.55
MCP-7	Bear Creek	2.92	1.64	3.44	5.81
MCP-7 rep.	Bear Creek	3.36		2.74	
MCP-8	Rio Lado Creek	3.50	2.02	0.91	4.32
MCP-9	Deadwood Creek	4.67	0.68	12.18	17.30
MCP-9 rep.	Deadwood Creek	5.06			
MCP-10	Mine Seep below Poor Boy Mine	0.98	0.41	47.90	26.89
MCP-10 rep.	Mine Seep below Poor Boy Mine	2.27			
MCP-11	Silver Creek near Mouth	4.25	0.75	206.49	103.04
MCP-11 rep.	Silver Creek near Mouth	5.45			
MCP-11B	Mine Seep on Silver Creek	5.44	4.38	8.01	202.80
MCP-12	Silver Creek below Mine Tailings	3.54	0.94	117.81	48.34
MCP-12 rep.	Silver Creek below Mine Tailings	3.68			
MCP-13	Mine Seep at former Sulfuric Acid Plant	2.18	0.73	44.64	95.10
MCP-13 rep.	Mine Seep at former Sulfuric Acid Plant	21.07			
MCP-14	Horse Creek	4.61	1.60	72.36	38.48
MCP-14 rep.	Horse Creek	4.92	1.50		55.87
MCP-15	Upper Mine Seep on Dolores River	1.46	0.45	14.37	284.21
MCP-15 rep.	Upper Mine Seep on Dolores River	1.52			
MCP-17	Dolores River at Big Bend Boat Launch	2.20	1.58		21.64
MCP-19	West Dolores R below Geyser Crk		1.71		16.62
MCP-21	Silver Creek - Upper		0.96		24.93
NAR-1	Unnamed trib., Narraguinnep	1.94	1.04	16.26	15.12
NAR-2	Ditch entering Narraguinnep NW corner	1.91	1.51	1.16	14.54
NAR-3	Pond/backwater in NW corner	1.90	0.73	18.42	<17

3.6 Mercury Concentrations and Water Quality in the Reservoirs

Mercury in Water and Sediment

Historical sampling of McPhee and Narraguinnep Reservoirs and their watersheds is summarized in Tetra Tech (2000). Data on mercury prior to 1999 are limited in number, did not use ultra-clean sampling and analysis, and are generally characterized by high detection limits. They are therefore of limited use in developing the TMDL.

Additional intensive sampling of the Reservoirs was conducted in June and August of 1999 using ultra-clean methods, as described in Tetra Tech (2000). These results are summarized briefly here. Sampling locations within the Reservoirs are shown in Figure 1-3.

The McPhee Reservoir water quality was alkaline with high dissolved oxygen in both June and August sampling. The total dissolved solids (TDS) were low (120 to 140 mg/L in June and 120 to 270 mg/L in August). The major ions were calcium (30 to 35 mg/L in June and 29 to 31 mg/L in August) and sulfate (23 to 27 mg/L in June and 17 to 19 mg/L in August), plus bicarbonate. Chloride was about 4 mg/L in both data sets. The iron concentrations were low, all less than 0.1 mg/L, which is consistent with the alkaline conditions and abundant dissolved oxygen. Dissolved organic carbon (DOC) was about the same in both events, 3 to 5 mg/L. Nutrients were low in both data sets, with more phosphorus in the June water samples. Chlorophyll *a* ranged from 0.006 to 0.016 mg/L in June and <0.001 mg/L in August. The higher phosphorus concentrations in June are thought to be related to the increased suspended solids in the Reservoir. The suspended solids in the Reservoir samples were higher in June (<5 to 10 mg/L) than in August (<5 mg/L, except for one sample that was 6 mg/L). At McPhee Reservoir, the Secchi depths ranged from 7.5 to 10.5 ft, which represented 15 to 25 percent of the total water depth at the sampling locations.

Vertical water column profiles for McPhee show that the Reservoir in June was weakly stratified with a temperature difference of about 4 °C between the surface and shallow depths of about 45 ft. The deepest profile showed a decrease in temperature from 14 °C at the surface to about 8 °C at a depth of 95 ft. The Reservoir in June had high dissolved oxygen concentrations throughout most of the profiles with low dissolved oxygen of 1 to 2 mg/L only in MCP-C between the depths of 40 and 80 ft. The August profiles showed increased stratification with a greater temperature difference between the surface and deeper water of about 11 °C in the deepest location at a depth of about 95 ft. The deeper water did not have dissolved oxygen less than 5 mg/L.

Narraguinnep Reservoir water quality was alkaline in both June and August of 1999. The total dissolved solids (TDS) were low (140 to 220 mg/L in June and 160 to 230 mg/L in August). The major ions were calcium (31 to 42 mg/L in June and 33 to 41 mg/L in August) and sulfate (25 to 61 mg/L in June and 32 to 78 mg/L in August), plus bicarbonate. Chloride was about 4 to 5 mg/L in both data sets. The iron concentrations were low, all less than 0.1 mg/L, which is consistent with the alkaline conditions and abundant dissolved oxygen. Dissolved organic carbon (DOC) was slightly higher in August (4 to 7 mg/L), compared to 3 to 4 mg/L in June. Nutrients were low in both data sets; phosphorus was detected only in the June water samples. The Reservoir was weakly stratified in June, but the dissolved oxygen was higher than 4 mg/L in all locations measured. The temperature difference in June in the deepest location was 6 °C between the surface and a depth of 50 ft. In August, there was increased stratification at some locations, such as NAR-A, where the dissolved oxygen decreased from about 9 mg/L at the surface to about 0 mg/L at a depth of 14 ft. The water sample collected at a depth of 11.5 ft had 3.83 mg/L of dissolved oxygen. Some of the other shallow locations were fully mixed, such as NAR-B and NAR-C with dissolved oxygen above 6 mg/L. The deepest profile showed a temperature difference of about 5 °C between the surface and a depth of 40 ft and decreased dissolved oxygen from about 8 mg/L to about 5 mg/L. The dissolved organic carbon concentrations increased slightly from 3 to 4 mg/L in the June samples to 4 to 7 mg/L in the August samples. Nitrate was below detection in both the June and August samples. Phosphorus was 0.01 to 0.04 mg/L in the June samples but below detection in the August samples. The suspended solids in the Reservoir samples were much higher in June (<5 to 52 mg/L) than in August (<5 to 6 mg/L).

Mercury sampling results for the water column of the two Reservoirs are summarized in Table 1-1. The June samples from McPhee showed greater mercury concentrations at depth than near the surface, and only deeper samples were collected in August. Average total mercury concentration in water was 1.6 ng/L, while the average methylmercury concentration was 0.027 ng/L.

The total mercury in Naraguinnep Reservoir samples varied from 0.74 to 2.07 ng/L in June and 0.6 to 0.97 ng/L in August (see Table 1-1), excluding the inlet area sample (NAR-C). The inlet area was lower in June (0.56 to 1.53 ng/L) than the other Reservoir samples but higher in August (1.85 ng/L). The dissolved mercury in June was higher in the inlet area (1.36 to 3.21 ng/L) than the other Reservoir samples (0.46 to 1.56 ng/L) and higher in August (1.06 ng/L in the inlet versus 0.4 to 0.67 ng/L in the other samples). The methylmercury was highest in the deepest sample at 26 ft (0.05 ng/L in June), compared to the inlet area (0.009 to 0.032 ng/L) or the other samples (<0.006 to 0.04 ng/L). Overall, the average total mercury concentration in water in Narraguinnep was 1.03 ng/L, while the average methylmercury concentration was 0.028 ng/L.

Table 1-1. Mercury in Water Column Samples, McPhee and Narraguinnep Reservoirs, 1999

Sample ID	Date	Unfiltered Total Mercury (ng/L)	Dissolved Total Mercury (ng/L)	Unfiltered Methylmercury (ng/L)	Dissolved Methylmercury (ng/L)
McPhee Reservoir					
MCP-A (3')	6/12/99	1.08	1.63	0.026	0.032
MCP-A (3') (rep)	6/13/99	1.76	NA	NA	NA
MCP-A (40')	6/12/99	1.99	1.36	0.045	0.022
MCP-B (3')	6/13/99	1.86	2.18	0.045	0.018
MCP-B (43')	6/13/99	2.46	1.64	0.030	0.035
MCP-C (3')	6/13/99	NA	1.12	0.045	0.021
MCP-C (43')	6/13/99	2.37	1.49	0.036	0.014
MCP-D (3')	6/13/99	1.73	1.36	0.023	0.017
MCP-D (43')	6/13/99	1.87	1.18	0.026	0.011
MCP-A (20')	8/9/99	0.88	0.56	0.031	<0.012
MCP-A (20') (rep)	8/10/99	1.22	0.78	0.012	0.017
MCP-A (35')	8/9/99	2.35	0.81	0.013	0.015
MCP-B (25')	8/10/99	0.87	0.67	0.014	0.012
MCP-B (40')	8/10/99	1.44	0.98	0.019	<0.012
MCP-C (25')	8/10/99	1.44	0.91	0.016	0.012
MCP-C (35')	8/10/99	1.56	1.01	0.034	0.017
MCP-D (25')	8/10/99	1.04	0.73	0.021	<0.012
MCP-D (40')	8/10/99	1.54	0.97	0.023	<0.012
Narraguinnep Reservoir					

NAR-A (1.5')	6/14/99	0.74	0.55	0.029	0.016
NAR-A (1.5') (rep)	6/15/99	0.80	0.46	0.018	0.026
NAR-A (13')	6/14/99	2.07	1.56	0.040	0.028
NAR-B (1.5')	6/15/99	0.75	0.62	0.031	<0.004
NAR-B (15')	6/15/99	0.94	0.63	<0.006	0.016
NAR-C (1.5')	6/15/99	1.53	1.36	0.009	0.032
NAR-C (6')	6/15/99	0.56	3.21	0.032	0.027
NAR-D (1.5')	6/15/99	1.12	0.51	<0.003	0.026
NAR-D (26')	6/15/99	1.49	0.70	0.050	0.026
NAR-A (3')	8/11/99	0.97	0.54	0.037	0.017
NAR-A (11.5')	8/11/99	0.85	0.45	0.032	<0.012
NAR-B (3')	8/11/99	0.90	0.40	0.025	0.021
NAR-B (8')	8/11/99	0.84	0.54	0.029	0.017
NAR-C (1.5')	8/11/99	1.85	1.06	0.022	0.025
NAR-D (20')	8/11/99	0.73	0.67	0.015	0.017
NAR-D (20') (rep)	8/11/99	0.60	0.63	0.020	<0.012
NAR-D (40')	8/11/99	0.73	0.56	0.028	0.015

Mercury sampling results for sediment are summarized in Table 1-2. In McPhee Reservoir, observed total mercury in sediment ranged from 13 to 131 ng/g. Methylmercury in sediment was low in all samples (less than 0.6 ng/g) and did not appear to be strongly correlated with total mercury concentration. In Narraguinnep Reservoir, total mercury in sediment ranged from 15 to 60 ng/g. Methylmercury concentrations in sediment were higher than those observed in McPhee, with a maximum of 1.2 ng/g. The highest methylmercury in the sediment in June and August was in the eastern part of the Reservoir, near the inlet from McPhee.

Table 1-2. Mercury in Sediment Samples, McPhee and Narraguinnep Reservoirs, 1999

Sample ID	Date	% Moisture	pH (S.U.)	Total Hg (ng/g) dry wt.	Methyl Hg (ng/g) dry wt.	TOC (%)	Sulfate (mg/kg – dry)	Sulfide-S (mg/kg – dry)
McPhee Reservoir								
MCP-A-B	6/12/99	71.6	-	63.50	0.232	3.05	-	191(55)
MCP-B-B	6/13/99	68.3	-	55.07	0.085	2.25	-	139
MCP-C-B	6/13/99	51.2	-	131.48	0.557	2.62	-	34
MCP-D-B	6/13/99	38.0	7.1	22.56	0.132	0.98	-	13
MCP-A-B	8/9/99	78.6	7.4	13.05	0.015	0.14	11	<5.1
MCP-A-B-rep	8/10/99	53.5	7.4	40.23	0.234	0.11	11	<5.4
MCP-B-B	8/10/99	46.0	6.4	62.69	0.198	0.62	18	20
MCP-C-B	8/10/99	64.4	6.5	28.89	0.145	0.61	360	<9.7
MCP-C-B-rep	8/10/99	64.4	-	34.49	-	-	-	-
MCP-D-B	8/10/99	52.2	6.7	39.07	0.377	0.99	17	28
Narraguinnep Reservoir								
NAR-A-B	6/14/99	32.9	-	26.64	1.187	0.90	-	179
NAR-A-B-rep	6/14/99	28.4	-	24.89	0.960	0.62	-	187
NAR-B-B	6/15/99	44.8	7.9	23.50	0.156	0.65	-	423
NAR-C-B	6/15/99	22.2	-	18.34	0.059	0.29	-	5
NAR-D-B	6/15/99	54.8	-	36.20	0.046	1.03	-	84(79)
NAR-A-B	8/11/99	67.9	6.7	28.70	0.337	0.73	9.8	<6
NAR-B-B	8/11/99	68.5	7.0	15.52	0.142	0.62	18	20

NAR-C-B	8/11/99	76.7	6.7	16.49	0.129(.128)	0.61	360	<6.2
NAR-D-B	8/11/99	49.2	6.7	55.25	0.168	0.38	53	1600
NAR-D-B-rep	8/11/99	52.3	6.8	59.70	0.185	0.35	51	44

Note: Results of replicates shown in parentheses.

Mercury in Biota

There is a wide variety of fish species found in McPhee Reservoir because of its large size and depth. Both warm and cold water fish species thrive in the Reservoir. The warm water gamefish species include the largemouth bass, smallmouth bass, northern pike, walleye, channel catfish, bluegill, crappie, yellow perch, and others. The cold water gamefish species include the McConaughy rainbow trout and Kokanee salmon. A 1993 creel survey showed that rainbow trout and Kokanee salmon accounted for 37 percent of the catch each, while smallmouth bass constituted 19 percent of the catch and yellow perch 6 percent. Largemouth bass and other species constituted less than 1 percent of catch. The Colorado Division of Wildlife (CDOW) has stocked over 4.5 million fish into McPhee Reservoir since it opened in 1986, including kokanee salmon, bluegill, channel catfish, large and smallmouth bass, and crappie (Montezuma Economic Development Council, 1997). Stocking of trout is conducted due to the lack of spawning habitat for trout and the fluctuating water levels. Trout are stocked in catchable sizes (9-12 inches) into the Reservoir each year. Most of the other fish species stocked into the Reservoir are introduced as fingerlings (2-4 inches in size). Native fish include the fathead minnow, green sunfish, bullhead, and yellow perch. The Reservoir has a reputation of being one of the best fishing spots in the area.

There are mostly warm water fish species found in Narraguinnep Reservoir; however, the Colorado Division of Wildlife occasionally stocks some rainbow trout into the Reservoir. The warm water gamefish species found in this Reservoir include northern pike, walleye, bass, bluegill, crappie, and channel catfish. The CDOW also periodically stocks fingerling walleye into the Reservoir.

Fish tissue samples were collected in McPhee and Narraguinnep Reservoirs on several occasions between 1988 and 1991. In 1988, three whole-body samples were collected from each of the Reservoirs. These samples showed that Narraguinnep, but not McPhee, had whole-body mercury concentrations in fish above 0.5 μg/g wet weight (Butler et al., 1995). The ranges of mercury in fish whole-body samples were 0.17 to 0.65 μg/g for Narraguinnep and 0.23 to 0.38 μg/g for McPhee. Two fillet samples were collected from McPhee (0.38 and 0.68 μg/g) and three fillet samples were collected from Narraguinnep (1.2 to 1.6 μg/g). One of the fillet samples from McPhee and all three from Narraguinnep exceeded 0.5 μg/g wet weight.

More extensive fish data were collected in 1989, 1990, and 1991 by CDOW and USFWS. These data are summarized in detail in Tetra Tech (2000). Most of the fish samples from McPhee were less than 0.5 μg/g. The range of mercury concentrations in the fish tissue was 0.08 μg/g in a composite Kokanee salmon sample from 1991 to 0.73 in a largemouth bass composite fillet sample from 1989, with four samples out of 25 above 0.5 μg/g wet weight (Table 4-1). These fish included two largemouth bass greater than 12 inches long, a 15-inch long smallmouth bass, and a 6-12-inch long black crappie. In May 1991 CDPHE established a fishing advisory for mercury in McPhee based on the elevated mercury concentrations observed in some largemouth bass samples.

The 1989-1991 fish tissue mercury concentrations reported for Narraguinnep ranged from 0.11 to 1.2 µg/g wet weight, all analyzed as fillets. As expected, the larger piscivorous fish, such as walleye and northern pike, had higher mercury concentrations than the non-piscivorous fish. Five of the nine samples had mercury concentrations above 0.5 µg/g, including walleye bigger than 12 inches long and northern pike bigger than 18 inches long. In May 1991 CDPHE established a fishing advisory for mercury in Narraguinnep based on the elevated mercury concentrations observed in some walleye and northern pike samples.

Additional fish samples were collected in 1999 and analyzed by ultra-clean methods. These are summarized in Table 1-3. The fish species analyzed at McPhee included smallmouth bass, black crappie, yellow perch, and rainbow trout. In McPhee Reservoir, the highest mercury concentrations were measured in a 14-inch smallmouth bass (0.993 µg/g with replicate value of 0.515) and a 15-inch smallmouth bass (0.65 µg/g). Of the thirty samples analyzed, only these two smallmouth bass samples exceeded a concentration of 0.5 µg/g. Mercury concentrations in the different species increased with size and were consistent with diet in that the piscivorous fish such as smallmouth bass had higher mercury than fish that eat primarily insects and benthic invertebrates such as yellow perch.

The fish species analyzed in Narraguinnep included channel catfish, northern pike, walleye, and yellow perch. The highest mercury concentrations were measured in a 17-inch walleye (1.5 µg/g) and a 16-inch walleye (0.8 µg/g). There was one fish above 1 µg/g and five above 0.5 µg/g, all walleye.

A variety of benthic invertebrates were also sampled in the Reservoirs in 1999, as discussed in Tetra Tech (2000). Four samples from McPhee Reservoir ranged from 6.4 to 22.06 ng/g total mercury, while four samples from Narraguinnep ranged from 4.60 to 18.10 ng/g total mercury.

The 1999 field sampling program confirmed that fish are present in both McPhee and Narraguinnep Reservoirs with mercury concentrations above 0.5 µg/g in fillet samples. Most of the fish with elevated tissue concentrations are large piscivorous fish.

Table 1-3. Fish Tissue Samples from McPhee and Narraguinnep Reservoirs, 1999

Fish Type	Sample No.	Length (in.)	Weight (g)	Total Mercury (µg/g wet wt.)	Methylmercury (µg/g - wet wt.)	Tissue Wt. (g)	P Mo
McPhee Reservoir							
Smallmouth bass	MP01	15.35	760	0.6432	0.7451	85	7
Smallmouth bass	MP02	13.98	560	0.4118	0.3280	84	7
Smallmouth bass	MP03	7.09	79	0.1212	0.1019	19	7
Smallmouth bass	MP04	9.06	145	0.2834	0.2153	22	7
Smallmouth bass	MP05	4.37	15	0.1295	0.1130	2.5	8
Smallmouth bass	MP06	13.78	650	0.5147	0.4090	110	7
Smallmouth bass	MP06 (rep.)	13.78	650	0.9930	0.4889	110	7
Smallmouth bass	MP07	7.09	70	0.1711	0.1302	25	7
Smallmouth bass	MP08	11.02	310	0.1808	0.1693	50	7
Smallmouth bass	MP09	9.84	170	0.1978	0.1939	25	8
Smallmouth bass	MP10	12.60	440	0.2623	0.2514	65	7
Smallmouth bass	MP10 (rep.)	12.60	440	0.2597	NA	65	7
Black crappie	MP11	5.91	55	0.0832	0.0890	15	7
Black crappie	MP12	4.33	18	0.0733	0.0713	6	7
Black crappie	MP13	6.10	62	0.1146	0.1237	10	7
Yellow perch	MP14	6.30	55	0.1480	0.1557	9	7
Yellow perch	MP15	7.87	110	0.1416	0.1576	20	7
Yellow perch	MP16	6.50	68	0.2294	0.2334	10	7
Yellow perch	MP17	5.71	36	0.1629	0.1458	6	7
Yellow perch	MP18	5.91	50	0.1223	0.1031	7	7
Yellow perch	MP19	5.12	28	0.1112	0.0942	4	7
Yellow perch	MP20	4.72	18	0.0743	0.0794	3	7
Yellow perch	MP21	6.69	70	0.1665	NA	12	7
Yellow perch	MP22	7.09	90	0.1176	NA	14	7
Yellow perch	MP23	4.37	15	0.1140	NA	2	7
Rainbow trout	MP24	8.07	84	0.0308	NA	15	8

Fish Type	Sample No.	Length (in.)	Weight (g)	Total Mercury (µg/g wet wt.)	Methylmercury (µg/g - wet wt.)	Tissue Wt. (g)
Table 1-3. (Continued)						
Rainbow trout	MP25	9.06	126	0.0264	NA	22
Rainbow trout	MP26	10.63	215	0.3078	NA	40
Rainbow trout	MP27	8.86	125	0.0268	NA	24
Rainbow trout	MP28	8.66	105	0.0280	NA	16
Rainbow trout	MP29	8.27	84	0.0392	NA	12
Rainbow trout	MP30	8.27	105	0.0246	NA	17
Narraguinnep Reservoir						
Walleye	NR01	18.11	1000	0.5914	NA	185
Walleye	NR02	16.93	750	0.5811	NA	104
Walleye	NR03	14.17	380	0.3435	NA	78
Walleye	NR04	13.39	340	0.3084	NA	62
Walleye	NR05	16.93	650	1.4977	NA	118
Walleye	NR06	16.14	625	0.7400	NA	125
Walleye	NR06 (rep.)	16.14	625	0.7416	NA	125
Walleye	NR07	15.35	550	0.5430	NA	105
Walleye	NR08	11.02	170	0.1709	NA	25
Northern pike	NR09	18.90	600	0.2215	NA	110
Northern pike	NR10	20.08	700	0.4197	NA	148
Yellow perch	NR11	11.42	400	0.1736	NA	55
Yellow perch	NR11 (rep.)	11.42	400	0.1736	NA	55
Yellow perch	NR12	11.81	455	0.1744	NA	85
Yellow perch	NR13	11.02	320	0.1250	NA	60
Yellow perch	NR14	13.58	580	0.2793	NA	100
Yellow perch	NR15	9.45	250	0.1152	NA	39
Yellow perch	NR16	7.09	85	0.1387	NA	20
Yellow perch	NR17	8.66	170	0.1397	NA	27
Yellow perch	NR18	7.48	95	0.0904	NA	16
Yellow perch	NR19	11.22	240	0.1512	NA	64

Fish Type	Sample No.	Length (in.)	Weight (g)	Total Mercury (µg/g wet wt.)	Methylmercury (µg/g - wet wt.)	Tissue Wt. (g)	Perce Moist
Table 1-3. (Continued)							
Yellow perch	NR20	9.06	175	0.1342	NA	23	76.4
Channel catfish	NR21	24.02	2730	0.3595	NA	360	76.4
Channel catfish	NR22	23.62	2755	0.3371	NA	355	74.9
Channel catfish	NR23	19.49	1420	0.3663	NA	170	62.9
Channel catfish	NR24	16.54	885	0.3027	NA	85	73.9
Channel catfish	NR25	23.43	2445	0.4374	NA	265	75.8
Channel catfish	NR26	20.47	1640	0.3101	NA	140	68.7
Yellow perch	NR27	11.22	415	0.1619	NA	82	74.8
Yellow perch	NR28	10.43	305	0.1378	NA	60	76.1
Yellow perch	NR29	7.87	130	0.1284	NA	23	77.4
Yellow perch	NR30	7.87	125	0.1046	NA	22	77.4

4. Linkage Analysis

The linkage analysis defines the connection between numeric targets and identified pollutant sources. The linkage is defined as the cause-and-effect relationship between the selected indicators, the associated numeric targets, and the identified sources. This provides the basis for estimating total assimilative capacity and any needed load reductions. Specifically, models of watershed loading of mercury are combined with a model of mercury cycling and bioaccumulation in the lake. This enables a translation between the numeric target (expressed as a fish tissue concentration of mercury) and mercury loading rates. The loading capacity is then determined via the linkage analysis as the mercury loading rate that is consistent with meeting the target fish tissue concentration.

To develop the linkage analysis it is first necessary to consider important processes that control mercury cycling and bioaccumulation. A key issue for the linkage analysis for a lake mercury TMDL is that fish tissue concentrations may not be directly predictable from external mercury loads alone. Instead, in-lake processes controlling water chemistry and consequent effects on mercury speciation and cycling may play a key role in determining the rate of mercury bioaccumulation and resulting fish tissue concentration associated with a given loading rate. In particular, methylmercury concentrations in surface water and in shallow sediment areas where fish feed, rather than total mercury load to the lake, will drive mercury bioaccumulation. The linkage analysis therefore requires use of coupled models that (1) estimate mercury loading to the Reservoirs and (2) predict mercury cycling and speciation within the lakes.

Section 4.1 provides an overview of the mercury cycle. Section 4.2 then provides an overview of the structure of the watershed loading component of the proposed linkage analysis. This section is followed by additional sections that describe the various components of the watershed and lake modeling effort.

4.1 The Mercury Cycle

Development of the linkage analysis requires an understanding of how mercury cycles in the environment. Mercury chemistry in the environment is quite complex. Mercury has the properties of a metal (including great persistence due to its inability to be broken down), but also has some properties of a hydrophobic organic chemical due to its ability to be methylated through a bacterial process. Methylmercury is easily taken up by organisms and tends to bioaccumulate; it is very effectively transferred through the food web, magnifying at each trophic level. This can result in high levels of mercury in organisms high on the food chain, despite nearly unmeasurable quantities of mercury in the water column. In fish, mercury is not usually found in levels high enough to cause the fish to exhibit signs of toxicity, but wildlife that habitually eat contaminated fish are at risk of accumulating mercury at toxic levels, and the mercury in sport fish can present a potential health risk to humans.

Selected aspects of the lake and watershed mercury cycle are summarized schematically in Figure 4-1, based on the representations discussed in Hudson et al. (1994), Park (1996), and

Tetra Tech (1999c). The boxes represent stores of mercury, and the arrows represent fluxes. The top of the diagram summarizes the various forms of mercury that may be loaded to a lake.

It is important to recognize that mercury exists in a variety of forms, including elemental mercury (Hg(0)), ionic mercury (Hg(I) and Hg(II)), and compounds in which mercury is joined to an organic molecule.

In Figure 4-1, Hg(I) is ignored because Hg(II) species generally predominate in aquatic systems. Mercuric sulfide (HgS or cinnabar) is a compound formed from Hg(II) but is shown separately because it is the predominant natural ore. Organic forms of mercury include methylmercury (CH_3Hg or "MeHg"), and also other organic forms, including natural forms such as dimethylmercury and man-made compounds such as organic mercury pesticides. (Where sorption and desorption are indicated in the model diagram, "Hg(II)" and "MeHg" refer to the same common pools of water column Hg(II) and MeHg shown in the compartments at the top of the diagram.)

In the lake mercury cycle, it is critical to consider the distribution of mercury load between the various forms. The major forms reaching a lake from the watershed can have different behavior:

- Mercuric sulfide (HgS), which can be washed into the lake as a result of weathering of natural cinnabar outcrops. HgS has low solubility under typical environmental conditions and would be expected to settle out to the bottom sediments of the lake. Under aerobic conditions, however, Hg(II) may be liberated by a bacteria-mediated oxidation of the sulfide ion. This Hg(II) would then be much more bioavailable and would be available for methylation. Alternatively, under anaerobic conditions, HgS may be formed from Hg(II).

- Methylmercury (MeHg), which is found in rainfall and may be found in small amounts in mine tailings or wash sediments. It is more soluble than HgS and has a strong affinity for lipids in biotic tissues.

- Elemental mercury (Hg(0)), which may remain in mine tailings, as has been noted in tailings piles from recent gold mining in Brazil. Elemental mercury tends to volatilize into the atmosphere, though some can be oxidized to Hg(II).

- Other mercury compounds that contain and may easily release ionic Hg(II). Such compounds are found in the fine residue left at abandoned mine sites where mercury was used to draw gold or silver out of pulverized rock.

Note that dimethylmercury (CH_3-Hg-CH_3) is ignored in the conceptual model shown in Figure 4-1, because this mercury species seems to occur in measurable quantities only in marine waters. Organic mercury pesticides also have been ignored in this TMDL study, because such pesticides are not currently used in this country and past use is probably insignificant as there is little cropland in the McPhee watershed.

Mercury and methylmercury form strong complexes with organic substances (including humic acids) and strongly sorb onto soils and sediments. Once sorbed to organic matter, mercury can be ingested by invertebrates, thus entering the food chain. Some of the sorbed mercury will settle to the lake bottom; if buried deeply enough, mercury in bottom sediments will become unavailable to the lake mercury cycle. Burial in bottom sediments can be an important route of removal of mercury from the aquatic environment.

Methylation and demethylation play an important role in determining how mercury will accumulate through the food web. Hg(II) is methylated by a biological process that appears to involve sulfate-reducing bacteria. Rates of biological methylation of mercury can be affected by a number of factors. Methylation can occur in water, sediment, and soil solution under anaerobic conditions, and to a lesser extent under aerobic conditions. In lakes, methylation occurs mainly at the sediment-water interface and at the oxic-anoxic boundary within the water column. The rate of methylation is affected by the concentration of available Hg(II) (which can be affected by the concentration of certain ions and ligands), the microbial concentration, pH, temperature, redox potential, and the presence of other chemical processes. Methylation rates appear to increase at lower pH. Demethylation of mercury is also mediated by bacteria.

Both Hg(II) and methylmercury (MeHg) sorb to algae and detritus, but only the methylmercury is assumed to be passed up to the next trophic level (inorganic mercury is relatively easily egested). Invertebrates eat both algae and detritus, thereby accumulating any MeHg that has sorbed to these. Fish eat the invertebrates and either grow into larger fish (which continue to accumulate body burdens of mercury), are eaten by larger fish or other piscivores, or die and decay. At each trophic level, a bioaccumulation factor must be assumed to represent the magnification of mercury concentration that occurs as one steps up the food chain.

Typically, almost all of the mercury found in fish (greater than 95 percent) is in methylmercury form. Studies have shown that fish body burdens of mercury increase with increasing size or age of the fish, with no signs of leveling off.

Although it is important to identify sources of mercury to the lakes, there may be fluxes of mercury within the lake that would continue nearly unabated for some time even if all sources of mercury to the lake were eliminated. In other words, compartments within the lake are probably currently storing a significant amount of mercury, and this mercury can continue to cycle through the system (as shown in the conceptual diagram, Figure 4-1) even without an ongoing outside source of mercury. The most important store of mercury within the lake is likely to be the bed sediment. Mercury in the bed sediment may cause exposure to biota by being:

- Resuspended into the water column, where it is ingested or it adsorbs to organisms that are later ingested.

- Methylated by bacteria. The methylmercury tends to attach to organic matter, which may be ingested by invertebrates and thereby introduced to the lake food web.

4.2 Structure of the Watershed Loading Component for the TMDL

While mercury load can originate from a wide variety of source types, information to characterize many of these sources is limited. Lake and stream water and sediment monitoring for mercury in the McPhee and Narraguinnep watersheds by modern ultra-clean analytical methods consists primarily of the two sampling events conducted by Tetra Tech in June and August 1999 (Tetra Tech, 2000). There appear to be consistent differences in concentrations between the two sampling events. These sampling events achieved good spatial coverage, but two points in time is not enough to establish reliable averages, and cannot resolve seasonal trends.

How are the limited available data best used to characterize mercury loading? Because ionic mercury is particle-reactive, much of the mercury within streams is associated with the sediments and moves through the watershed during major sediment scour events. A large fraction likely moves as bedload. At other times, smaller amounts of mercury move in dissolved form or associated with suspended sediment. Dissolved mercury associated with seeps and point sources might predominate during low flow periods. Given the available data, it is useful to consider three components of watershed transport of mercury: dissolved and suspended mercury during non-snowmelt conditions; dissolved and suspended mercury derived from melt of the winter snowpack; and bedload transport of particulate mercury.

The stream sediment mercury concentration can likely be assumed to be relatively stable in time, although highly variable in space. Thus, the two sample rounds are likely adequate to characterize sediment concentrations. Two sampling events do not provide a very clear basis for inference regarding long-term average water column loads because water concentrations are likely much more variable in time. Analysis of the water column observations for McPhee streams shows higher concentrations of total unfiltered and total dissolved mercury in June samples than in August samples at all stations that were sampled during both events. This could reflect higher suspended sediment concentrations (with re-equilibration causing secondary increases to the dissolved concentrations) during the June sampling, but suspended sediment concentrations were not monitored. Another cause could be seasonal changes in the source area of flow responsible. If August has a greater dominance by ground water base flow pathways this could also lead to lower concentrations. There does not appear to be enough evidence available to clearly resolve this issue. A simple approach is to assume that the average of the water column samples reported in Tetra Tech (2000) provides a "best available" estimate of the (exclusively) water column transport, while observed surface sediment concentrations provide an indication of the mercury moving in sediment bedload transport. This could lead to some double counting, to the extent that the June samples include particle-associated mercury mobilized from the sediment; however, any double counting is expected to be small relative to total mercury transport, and, if present, is expected to err on the side of conservatism.

Accordingly, the watershed ("external") loading of mercury is estimated using three components, described below. Each of these components is assessed on a geographic basis, and tied to individual source areas where data allow.

1. Non-snowmelt loading of dissolved and suspended particulate mercury. The non-snowmelt portion of the water column transport of mercury is estimated from the average of total mercury concentrations in June and August Tetra Tech sampling coupled with an analysis of flow.

2. Snowmelt loading of dissolved and suspended particulate mercury. Mercury transport is potentially enhanced during the melt of the winter snowpack, as this may release atmospheric deposition load accumulated and stored over the winter. Water loads during snowmelt include the "normal" water load, plus any additional amounts from the snowpack. As noted below, this component does not appear to be a significant source of mercury load to McPhee or Narraguinnep Reservoir.

3. Watershed sediment-associated mercury load. Much of the mercury load from the watershed likely moves in association with sediment during a few high flow scour events. The available sampling represents this mercury in terms of concentrations in bed sediments. Sufficient data are not available to calibrate a model of sediment transport in the watersheds. An approximate approach is therefore used, based on an assumption of long-term dynamic equilibrium in stream channels. This approach, which was successfully used in the TMDL studies for Arivaca and Peña Blanca Lakes in Arizona (Tetra Tech, 1999a; 1999b), makes the following arguments:

- The amount of sediment moving through the major streams is equivalent (as a long-term average) to the rate of sediment loading to those streams, as estimated by a sediment load model.
- The concentration of mercury in sediment moving through the system is equivalent to the concentration measured in stream sediment samples.
- Mercury may be treated as approximately conservative in the stream sediments.

Each of these assumptions is a rough approximation only; however, they may be combined to provide an order-of-magnitude estimate of sediment-associated mercury delivery. The watershed load estimates implicitly account for the net effects of atmospheric deposition onto the watershed and its snowpack.

4.3 Watershed Hydrologic and Sediment Loading Model

An analysis of watershed loading could be conducted at many different levels of complexity, ranging from simple export coefficients to a dynamic model of watershed loads. Data are not, however, available at this time to specify parameters or calibrate a detailed representation of flow and sediment delivery within the watersheds. Therefore, a relatively simple, scoping-level analysis of watershed mercury load, based on an annual mass balance of water and sediment loading from the watershed, is used for the TMDL. Uncertainty introduced in the analysis by use of a simplified watershed loading model must be addressed in the Margin of Safety.

4.3.1 Model Selection

Watershed-scale loading of water and sediment was simulated using the Generalized Watershed Loading Function (GWLF) model (Haith et al., 1992). The complexity of this loading function model falls between that of detailed simulation models, which attempt a mechanistic, time-dependent representation of pollutant load generation and transport, and simple export coefficient models, which do not represent temporal variability. GWLF provides a mechanistic, simplified simulation of precipitation-driven runoff and sediment delivery, yet is intended to be applicable as a scoping tool without formal calibration. Solids load, runoff, and ground water seepage can then be used to estimate particulate and dissolved-phase pollutant delivery to a stream, based on pollutant concentrations in soil, runoff, and ground water.

GWLF simulates runoff and streamflow by a water-balance method, based on measurements of daily precipitation and average temperature. Precipitation is partitioned into direct runoff and infiltration using a form of the Natural Resources Conservation Service (NRCS) Curve Number method. The Curve Number determines the amount of precipitation that runs off directly, adjusted for antecedent soil moisture based on total precipitation in the preceding five days. A separate Curve Number is specified for each land use by hydrologic soil grouping. Infiltrated water is first assigned to unsaturated zone storage, where it may be lost through evapotranspiration. When storage in the unsaturated zone exceeds soil water capacity, the excess percolates to the shallow saturated zone. This zone is treated as a linear reservoir that discharges to the stream or loses moisture to deep seepage, at a rate described by the product of the zone's moisture storage and a constant rate coefficient.

Flow in rural streams may derive from surface runoff during precipitation events or from ground water pathways. The amount of water available to the shallow ground water zone is strongly affected by evapotranspiration, which GWLF estimates from available moisture in the unsaturated zone, potential evapotranspiration, and a cover coefficient. Potential evapotranspiration is estimated from a relationship to mean daily temperature and the number of daylight hours.

Monthly sediment delivery from each land use is computed from erosion and the transport capacity of runoff, whereas total erosion is based on the universal soil loss equation (Wischmeier and Smith, 1978), with a modified rainfall erosivity coefficient that accounts for the precipitation energy available to detach soil particles (Haith and Merrill, 1987). Thus, erosion can occur when there is precipitation but no surface runoff to the stream; delivery of sediment, however, depends on surface runoff volume. Sediment available for delivery is accumulated over a year, although excess sediment supply is not assumed to carry over from one year to the next.

4.3.2 GWLF Model Input

The GWLF application requires information on land use distribution, meteorology, and parameters that govern runoff, erosion, and nutrient load generation. Four primary data sources were used to develop the model parameters used for the watershed simulations; 1) Digital

Elevation Models (DEMs), 2) Land Use/ Land Cover geographic coverages, 3) soil characteristics databases, and 4) meteorological data. The USDA ARS Soil and Water Assessment Tool (SWAT) ArcView interface (AV SWAT) was used to estimate many of the runoff and erosion parameter values required by the GWLF model directly from GIS data (Neitsch and DiLuzio, 1999). This interface was selected because it can incorporate high-resolution DEM, land use, and soil GIS coverages and is designed to estimate many of the same parameters required by GWLF. The SWAT model itself was evaluated, but not selected for application to the Colorado reservoirs for the following reasons:

- The SWAT ArcView interface was in beta release at the time of the analysis and had known errors and instabilities related to the creation of SWAT input files.
- Steep slopes and high soil rock content of some of the high-elevation portions of the McPhee watershed are outside the range of stated applicability of SWAT.
- Neither availability of data nor allocated resources were considered sufficient to calibrate the SWAT model, which is considerably more complete than GWLF.

Sub-basin Delineation

The watersheds were divided into sub-basins in order to isolate potential source areas and improve the accuracy of the GWLF simulation. Digital elevation model (DEM) coverages in a 1:100,000 30-meter resolution grid format were obtained from USGS (Figure 4-2). The watershed delineation tool with AV SWAT was used to distinguish the watershed boundaries based upon the DEM coverages and Reach File 3 hydrography. Appropriate watershed outlet points were selected based upon tributary confluences, availability of water quality monitoring locations, and to separate out expected source areas, such as known mining districts. A total of 12 sub-basins were defined for McPhee and 6 for Narraguinnep. These are shown in Figure 4-3.

Land Use/Land Cover

Because of the limited availability of recent GIS land use data for Colorado, building an optimum land use/land cover (LU/LC) input file for modeling of the watersheds required the acquisition, comparison, and combination of two distinct data sets. GIS land use/land cover data for Colorado were obtained from the U.S. Geological Survey (USGS) Geographic Information Retrieval and Analysis System (GIRAS) and from the Colorado Gap Analysis Project (GAP). These two GIS coverages for Colorado were created at different times for different purposes and, as a result, contain discrepancies which required resolution. The following is an outline of the differences between the two GIS coverages and the process by which those differences were resolved.

The USGS GIRAS land use/land cover GIS coverage is assembled in 1:250,000 scale quadrangle maps of the conterminous United States based on NASA high-altitude aerial photographs, and National High Altitude Photography (NHAP) program images. Land cover types within the data set are interpreted for polygons down to a minimum of 4-16 hectares depending on the specific cover, which results in minimum polygon widths of 200-400 meters with exceptions down to 92 meters for distinct major line features (e.g. rivers, interstate highways, etc.). Classification of the land cover types in GIRAS is based on the Anderson Classification System (Anderson et al., 1976). The GIRAS data set was created to depict LU/LC for a variety of purposes, including water quality analysis, growth management, and other types of environmental impact assessment. The data set for the state of Colorado is based on aerial reconnaissance performed from 1977 to 1980, and in addition to being somewhat outdated, the coverage has frequent errors regarding the interpretation of cover types. The GIRAS LU/LC data are distributed by EPA with the BASINS (Better Assessment Science to Integrate Nonpoint Sources) water quality modeling system from which the Colorado data were obtained for this analysis.

To assess the accuracy of the USGS GIRAS data and major land use changes that may have occurred since reconnaissance was performed for the GIRAS, LU/LC data were also obtained from the Colorado Gap Analysis Project (GAP). The Colorado GAP GIS coverage was produced in conjunction with the National GAP program for the purposes of quantifying major habitat types and predicting distributions of vertebrate animal species. The Colorado GAP data are also organized in 1:250,000 scale quadrangle maps which are based primarily on LandSat Thematic Mapper satellite imagery with Colorado scenes recorded between 1984 and 1990. The minimum unit area of interpretation for land cover polygons in the GAP data is 100 hectares in upland areas and 40 hectares in riparian areas. The classification system for the Colorado vegetation map is described in detail in the *Manual to Accompany the Gap Analysis Land Cover Map of Colorado* (Thompson et al., 1996). Land cover classifications for the primary vegetative community occupying each defined polygon are contained within the attribute tables for the Colorado GAP coverage and are each described in the accompanying metadata file. Colorado GAP data for this analysis were downloaded directly from the Colorado Natural Diversity Information Source website located at http://ndis.nrel.colostate.edu/.

The GIRAS data are based on imagery that is around 20 years old and has numerous errors in the interpretation of the land cover types. By contrast, the GAP data is based on much more recent reconnaissance and is less subject to error. However, due to the more coarse resolution of the GAP data, it often fails to depict land cover occurring on small parcels that are captured by GIRAS. The discrepancies produced by these contrasts between the two data sources are difficult to determine by evaluating their native formats due to significantly different land cover classification schemes. To facilitate comparison of the data sets the land cover types were aggregated into a simpler common scheme. This task was achieved through development of ArcView Avenue programs, which read the land cover classification attributes for each coverage and added a new aggregated classification for each polygon to the respective attribute files. For purposes of comparison all forest cover types in each data set were aggregated into a single category ("Forest"), all agricultural types into a single category ("Agriculture"), and so on, based on Level I of the Anderson Classification System (Anderson et al., 1976).

Comparison of the aggregated data sets for the McPhee and Narraguinnep watersheds showed that they are predominantly occupied by forest and rangeland. However, several areas of significant size within the McPhee watershed were found to have contradictory classifications in the two coverages. One of the areas of discrepancy consisted of a considerable portion of the lower end of the Bear Creek watershed that was classified as Cropland and Pasture in GIRAS and Mixed Forest in GAP. Through an interview with the USDA Natural Resource Conservation Service (NRCS) District Conservationist for Montezuma County, Bob Fuller (personal communication, February 2000), it was determined that the entire Bear Creek watershed was covered by timber. Mr. Fuller indicated that much of the timber in the lower portion of the watershed had been harvested in the late 1970s, the same time period for the GIRAS coverage, which may account for the misinterpretation of the land cover in the GIRAS data.

The second area of discrepancy consisted of a substantial portion of the watershed due northeast of McPhee Reservoir. GIRAS data classified the bulk of the northwest quarter of the watershed as rangeland whereas GAP classified the area as interspersed forest and rangeland parcels. Further input from Mr. Fuller revealed that several areas within this quadrant of the McPhee watershed were currently forested and that GAP data were likely to be more accurate in this area.

Despite the apparent errors in the GIRAS coverage, it was deemed more desirable than GAP data for modeling by virtue of its higher resolution. To improve the accuracy of the GIRAS, several forest cover polygons were updated from the GAP coverage. The amended GIRAS land use data for the McPhee and Narraguinnep watersheds are shown in Figure 4-4.

Soil Properties

Soil distribution and characteristics were obtained from the STATSGO soil coverage. The STATSGO database groups similar soils together into map units. Information such as taxonomic soil groups, water capacity, soil texture, and permeability are stored within the database for each map unit within the coverage. The distribution of the major soil groups for the McPhee/Narraguinnep watershed is presented in Figure 4-5. The union of the land use and watershed delineation themes was overlain on the STATSGO coverage to identify dominant soil groups and associated hydrologic soil classes across each land use type.

Meteorology

Hydrology in GWLF is simulated by a water-balance calculation, based on daily observations of precipitation and temperature. Precipitation in southwestern Colorado shows considerable local geographic variability, primarily due to orographic (elevation) effects, with higher precipitation at higher elevations. A search was made of available NOAA Cooperative Summary of the Day (SOD) reporting stations that (1) were in close proximity to the watersheds, and (2) had long periods of record without major data gaps. Table 4-1 presents the summary information for these stations. Figure 4-6 shows the locations of these stations.

Table 4-1. Selected Meteorological Stations

Station	Latitude	Longitude	Elevation (ft)	Available Data
Rico, CO COOP 052017	37.43	108.02	8,797	Precipitation Temperature
Dolores, CO COOP 052326	37.28	108.30	6,938	Precipitation
Yellow Jacket, CO COOP 059275	37.31	108.45	6,858	Temperature Precipitation
Lizard Head Pass, CO SNOTEL LIZC2	37.47	107.56	10,200	Precipitation Snowpack

Based on the review of available meteorological data, the most appropriate stations for watershed modeling appear to be the SOD stations at Rico and Dolores, Colorado. This selection was based on proximity to the watershed and completeness of data.

Online data were obtained for January 1980 to December 1998 from the Utah State University Climate Server (http://climate.usu.edu/free/USA_CO.htm). Additional data for February 1998 and calendar year 1999 were purchased from the Southwestern Regional Climate Center and the National Climatic Data Center. Any missing data were filled in from other stations, after adjusting for the average ratio between stations of precipitation and temperature. Gaps in rainfall measurements at the Rico station were filled primarily with data from the Dolores station. Data from the Yellow Jacket station were used if the Dolores station also had gaps during the same period. Similarly, gaps in the Dolores rainfall data were filled first with data from Rico and then with data from Yellow Jacket.

Average total precipitation and mean daily temperature by month for the 1980 to 1999 time period are summarized in Tables 4-2 and 4-3. Monthly precipitation is variable from year to year, as shown in Figure 4-7. The period of record retrieved contains both relatively wet periods (1982-1989) and dry periods (1994-1999). The Rico and Dolores stations, west of the Continental Divide, have, on average, low but relatively consistent precipitation year-round, with a drier period in April-June.

Table 4-2. Climate Normals for Rico, CO, 1980-1999

Month	Precipitation (In)	Minimum Air Temp (F)	Maximum Air Temp (F)	Median Air Temp (F)
January	2.3	6.4	38.6	22.5
February	2.6	9.7	40.3	25.0
March	2.8	14.6	43.5	29.0
April	1.7	21.6	50.5	36.1
May	1.9	28.6	59.6	44.1
June	1.6	34.2	70.1	52.1
July	3.1	40.0	74.0	57.0
August	3.2	39.2	71.7	55.5
September	2.7	32.7	65.5	49.1
October	2.1	24.5	56.3	40.4
November	2.3	14.9	44.3	29.6
December	1.9	7.7	39.2	23.4
Annual	**27.9**	**22.9**	**54.5**	**38.7**

Table 4-3. Climate Normals for Dolores (Precipitation) and Yellow Jacket, CO (Temperature), 1980-1999

Month	Precipitation (In)	Minimum Air Temp (F)	Maximum Air Temp (F)	Median Air Temp (F)
January	1.8	16.1	39.2	27.7
February	1.8	19.9	43.2	31.6
March	2.4	26.1	50.3	38.2
April	1.5	31.7	60.2	46.0
May	1.4	39.9	69.8	54.8
June	0.8	48.4	81.6	65.0
July	1.6	54.3	86.8	70.5
August	2.0	54.0	84.7	69.4
September	1.8	47.2	76.4	61.8
October	2.0	36.5	63.2	49.8
November	2.3	25.4	48.5	37.0
December	1.3	18.3	40.7	29.5
Annual	**20.4**	**34.9**	**62.1**	**48.5**

Differences in elevation between the subwatersheds and the meteorological stations were considered to have a significant effect on air temperature and precipitation. For this reason, the temperature and rainfall inputs to the model were adjusted using lapse rates and the difference in elevation between the subwatershed and meteorological station. Precipitation increases with elevation. Because precipitation is constrained to be non-negative, the precipitation lapse rate was represented as a multiplicative process. The analysis was based on comparison of the Dolores (6938'), Rico (8798'), and Lizard Head Pass SNOTEL (10,200') stations in the McPhee watershed. Between the elevations of Dolores and Rico, precipitation (in mm) is estimated from Dolores precipitation times 1.000642 dM, where dM is the increase in elevation in meters above Dolores. For elevations above Rico, precipitation is estimated from Rico precipitation times 1.000616 dM, where dM is the increase in elevation above Rico. Temperature lapse rate is assumed to be an additive, rather than multiplicative process, with temperature declining with elevation on average. Comparison of Yellow Jacket and Rico temperature records shows, on an average basis, a decrease of -9.26 °C per kilometer of elevation.

Water Balance Parameters

Runoff Curve Numbers. The direct runoff fraction of precipitation in GWLF is calculated using the curve number method from the U.S. Soil Conservation Service (now NRCS) TR55 method (SCS, 1986). This method is based on land use type and soil hydrologic group. Curve numbers can vary from 25 for undisturbed woodland with good soils to 100 for completely impervious surfaces. Weighted average curve numbers were calculated by AV SWAT for each land use/soil group category in each sub-basin.

Evapotranspiration Cover Coefficients. The portion of rainfall returned to the atmosphere is determined by GWLF based on temperature, type of vegetation, and the vegetation distribution. The evapotranspiration cover coefficient for each subwatershed was estimated by calculating an area weighted value based upon cover type. Evergreen forest and perennial crops such as pasture and range are given a constant coefficient of 1.0 throughout the year. Cover coefficients for annual crops and deciduous forests were set to 1.0 for the growing season and 0.3 for the nongrowing season.

Soil Water Capacity. Water stored in soil may evaporate, be transpired by plants, or percolate to ground water below the rooting zone. The amount of water that can be stored in soil and is available to plants—the soil's available water capacity—varies by soil type and rooting depth. Average available water capacity for each STATSGO soil type was calculated as the average of the fractional water capacities for the first two soil layers, multiplied by an assumed rooting depth of 100 cm, as recommended in the GWLF manual. Spatial weighted averages then yield available soil water capacities by model sub-basin. Given the low precipitation and high temperatures in the watershed, the available soil water capacity is infrequently exceeded in most of the deeper soils, with the result that the model predicts that most streamflow occurs as surface runoff of rainfall or melting snow.

Recession and Seepage Coefficients. The GWLF model has three subsurface zones: a shallow unsaturated zone, a shallow saturated zone, and a deep aquifer zone. Behavior of the second two stores is controlled by a ground water recession and a deep seepage coefficient. Because the model simulation yields almost no shallow ground water flow, results are insensitive to specification of these parameters. AV SWAT estimated a default recession coefficient of 0.048 per day, while the deep seepage coefficient was set to 0.

Erosion Parameters

GWLF simulates rural soil erosion using the Universal Soil Loss Equation (USLE). This method has been applied extensively, so parameter values are well established. This computes soil loss per unit area (sheet and rill erosion) at the field scale by:

$$A = RE \cdot K \cdot (LS) \cdot C \cdot P$$

where:

A = rate of soil loss per unit area,

RE = rainfall erosivity index,

K = soil erodibility factor,

LS = length-slope factor,

C = cover and management factor, and

P = support practice factor.

It should be noted that use of the USLE approach will likely underestimate total sediment yield in a watershed of this type. This is because the USLE addresses only sheet and rill erosion, whereas mass wasting (landslides) and gullying are probably the dominant components of the total sediment budget within the watershed. It was reasoned, however, that the mercury from the watershed that is likely to become bioavailable in the lake would be the mercury associated with the fine sediment fraction. The USLE approach should provide a reasonable approximation of the finer sediment load, even though movement of larger material by other processes is omitted, and can thus serve as a basis for evaluation of mercury loading from watershed sediments to the lake.

Soil loss or erosion at the field scale is not equivalent to sediment yield because substantial trapping may occur, particularly during overland flow or in first-order tributaries or impoundments. GWLF accounts for sediment yield by (1) computing transport capacity of overland flow and (2) employing a sediment delivery ratio (DR) that accounts for losses to sediment redeposition.

Rainfall Erosivity (RE). Rainfall erosivity accounts for the impact of rainfall on the ground surface, which can make soil more susceptible to erosion and subsequent transport. Precipitation-induced erosion varies with rainfall intensity, which shows different average characteristics according to geographic region. The factor is used in the USLE and is determined in the model as follows:

$$RE_t = 64.6 \cdot a_t \cdot R_t^{1.81}$$

where:

RE_t = rainfall erosivity (in megajoules mm/ha-h),

a_t = location- and season-specific factor, and

R_t = rainfall on day t (in cm).

Erosivity was assigned a value of 0.22 for April through September and 0.11 for October through March, based on New Mexico data reported by Selker et al. (1990).

Soil Erodibility (K) Factor. The soil erodibility factor indicates the propensity of a given soil type to erode, and is a function of soil physical properties and slope. Soil erodibility factors were extracted from the STATSGO soil coverage. Values for individual soils ranged from 0.01 to 0.32.

Length-Slope (LS) Factor. Erosion potential varies by slope as well as soil type. Length-slope factors were calculated by measuring representative slopes from topographic maps for upland and bottomland land-use categories. The LS factor is calculated by AV SWAT, following Wischmeier and Smith (1978), as:

$$LS = (0.045 \cdot x_k)^b \cdot (65.41 \, . \, \sin^2\Phi_k + 4.56 \cdot \sin^2\Phi_k + 0.065)$$

where:

$\Phi_k = \tan^{-1}(ps_k/100)$, where ps_k is percent slope, and

x_k = slope length (m).

LS values for individual land use varied from 1.35 to 6.62.

Cover and Management (C) and Practice (P) Factors. The mechanism by which soil is eroded from a land area and the amount of soil eroded depends on soil treatment resulting from a combination of land uses (e.g., forestry versus row-cropped agriculture) and the specific manner in which land uses are carried out (e.g., no-till agriculture versus non-contoured row cropping). Land use and management variations are represented by cover and management factors in the USLE and in the erosion model of GWLF. Cover and management factors were drawn from several sources (Wischmeier and Smith, 1978; Haith et al., 1992; Novotny and Chesters, 1981). Cover factors were 0.001 for forest, 0.003 for pasture, and 0.05 for rangeland, and reflect the relatively sparse cover typical of this landscape. Given the small amount of cropland in the watersheds, practice (P) factors were all set to 1, consistent with recommendations for non-agricultural land. The runoff and erosion parameter estimates used for the watershed model are presented in Table 4-4.

Table 4-4. Erosion and Sediment Yield Parameter Ranges

Land Use	CN	K	LS	C	P	KLSCP
Rangeland	61 - 89	0.01 - 0.37	0.36 - 6.26	0.05	1	0.0001 - 0.1002
Pasture	49 - 84	0.01 - 0.37	3.64 - 6.26	0.003	1	0.0001 - 0.0061
Evergreen Forest	55 - 77	0.01 - 0.32	0.36 - 6.26	0.001	1	0.0001 - 0.0022
Deciduous Forest	60 - 79	0.01 - 0.37	0.36 - 6.26	0.001	1	0.0001 - 0.0022
Barren	98	0.01 - 0.37	3.38 - 6.26	0.001	1	0.0001 - 0.0022

Sediment Delivery Ratio. The sediment delivery ratio (DR) indicates the portion of eroded soil carried to the watershed mouth from land draining to the watershed. The soil can be water-column suspended sediment or bedload, depending on the total size of the subwatershed. Values for DR were estimated from an empirical relationship of DR to watershed area (ASCE, 1975). ASCE's graphical relationship is approximated by the following empirical equation:

$$\mathrm{Log}_{10}(\mathrm{DR}) = -0.301 \ \mathrm{Log}_{10}(\mathrm{Area}) - 0.400$$

For lakes, it is not usually appropriate to calculate a DR based on total watershed area, since the watershed drains to the lake as a number of smaller, independent watersheds. The sediment delivery ratios were therefore calculated by delineating major subwatersheds for the lake and calculating a DR for each. The range of watershed areas and associated delivery ratios for the study areas are presented in Table 4-5.

Table 4-5. Watershed Sediment Delivery Ratios

Watershed	Total Area (km^2)	Subwatershed Areas (km^2)	Delivery Ratio
McPhee	2,097.7	18 - 322	0.070 - 0.167
Narraguinnep	24.3	1.8 - 12.0	0.188 - 0.334

4.3.3 Watershed Model Results

The GWLF flow and sediment model was run for the period from May 1981 through April 1999 for the McPhee and Narraguinnep watersheds. Of these watersheds, only McPhee is partially gaged. Minor adjustments were made to model parameters to better reflect annual runoff totals in the McPhee watershed, but the model is not formally calibrated. A comparison between model monthly average flows and gage records for the period of simulation was performed for the McPhee watershed to confirm that the model was producing results that were reasonable for Southwestern Colorado. Figure 4-8 compares the average monthly runoff for the watershed area above Dolores to the monthly average of the USGS gage records. Over the 19 years of simulation, model predictions capture the general trend in average monthly flows but do not exactly replicate observations. Results for individual years with "typical" flows were generally quite close to observations, and most of the error is accumulated from high flow years in the record. In most months, the model on average over-predicts gaged streamflow. This likely reflects the fact that the model does not account for transmission losses, diversions, and retention in small impoundments. No gage data are available for Narraguinnep watershed inflows.

The GWLF water and sediment simulation results were judged to provide sufficient accuracy for the intended purpose of initial mercury load estimation, although the over-prediction of average flows is likely to result in a high bias in the estimation of the water column mercury loads. The need for refinement of the watershed model will be evaluated based on the relative significance of this load component.

Sufficient data are not available to calibrate a model of sediment transport in the watersheds. The individual runoff and sediment estimates for the watersheds are shown in Tables 4-6 and 4-7.

Table 4-6. Individual Sub-basin Runoff and Erosion Estimates for McPhee Watershed

Sub-basin	Streamflow (L)	Sediment (kg)
1	1.46E+11	1.39E+06
2	1.42E+10	4.96E+05
3	1.71E+11	2.91E+05
4	1.88E+11	2.20E+06
5	6.9E+10	3.37E+05
6	6.08E+10	2.63E+06
7	3.05E+10	9.59E+05

8	5.47E+10	1.81E+06
9	4.19E+10	1.33E+05
10	8.03E+10	4.94E+05
11	6.15E+10	1.07E+05
12	3.52E+10	1.01E+06
Total	**9.53E+11**	**1.18E+07**

Table 4-7. Individual Sub-basin Runoff and Erosion Estimates for Narraguinnep Watershed

Sub-basin	Streamflow (L/yr)	Sediment (kg/yr)
1	1.85E+08	1.39E+06
2	1.45E+08	5.52E+04
3	9.04E+08	9.75E+04
4	2.33E+08	1.90E+03
5	2.53E+08	1.00E+02
6	1.70E+08	2.10E+03
Diversion from McPhee Reservoir	1.68E+11	~0.00E+00
Total	**1.70E+11**	**3.10E+06**

Note: Only a portion of the water diverted from McPhee into the Narraguinnep watershed actually reaches Narraguinnep Reservoir. The remainder is distributed to users by MVIC.

4.4 Watershed Mercury Loading Model

Estimates of watershed mercury loading are based on the flow and sediment loading estimates generated by GWLF through application of observed mercury concentrations. The observed concentrations were collected in 1999 and are described in Section 3.5. Much of the mercury load from the watersheds moves in association with sediment during high flow scour events. Instream loadings were calculated by multiplying the observed mercury concentrations by estimated streamflow for the watershed area above the monitoring point. Similarly, the sediment associated load was calculated by applying a sediment potency factor expressed as the mass of mercury per mass of sediment to the total estimated sediment load. Runoff and erosion estimates for individual watersheds were aggregated at tributary confluences to determine the total upstream load.

Ultimate sources of mercury in the watershed include release from the parent rock, mercury residue from mine tailings and seeps, point source discharges, and atmospheric deposition onto the watershed, including deposition and storage in snowpack. Monitoring in streams and stream sediments typically reflects the combined impact of a number of these sources. Estimated mercury loads transported in the water column were calculated by multiplying the estimated annual runoff volume by the average observed water column concentration. Sediment scour and bedload transport of mercury was calculated by multiplying sediment yield estimates by the average sediment concentration at a station of the two sample points for each station.

For the Narraguinnep watershed, direct watershed loading to the lake is simply the sum of loading from individual watersheds. This is not the case in the more complex McPhee watershed, where subwatersheds drain one into another before reaching the lake. In these watersheds, a sediment or water column sample at one point represents the net effects of all upstream areas, and several sample points may be present in sequence along a given path to the lake. The analyses of the McPhee data thus begins with the assessment of cumulative loads at specific monitored nodes within the watershed, as shown for McPhee in Table 4-8.

Unfortunately, the Dolores River mainstem was sampled at only a few points, so individual load estimates cannot be obtained from monitoring from sub-basins 1, 3, and 5, among others (see Figure 4-3 for sub-basin locations). Table 4-8 also provides direct estimates for two unmonitored sub-basins (6 and 8), which are not suspected to contain significant source areas (Tetra Tech, 2000). Loads in these sub-basins are estimated based on the median or central tendency of concentrations observed in other stations (excluding those stations identified as mine seeps or wastewater ponds).

Once the cumulative loads at each node are established, estimates of loading from individual sub-basins that are not monitored headwater basins are established by differencing. For instance, monitoring at Station MP-4 represents the net load derived from sub-basins 4 and 10. Subtracting the sub-basin 10 load from this sum yields an estimate of direct load from sub-basin 4.

In the case of node 5, the sampling station represents the cumulative effect of five upstream sub-basins, only two of which (2 and 11) are headwaters basins that were directly monitored. Estimates above this node were developed by assuming that direct load from sub-basin 5 (which does not have significant potential source areas identified in Tetra Tech, 2000) can be calculated from median concentrations. With this assumption, the total transport at node 5 minus the estimated loading for sub-basins 2, 11, and 5, yields an estimate of the net loading from sub-basins 1 and 3, which represent the upper Dolores River near Rico. Numerous potential mining sources are known in both sub-basins 1 and 3 (Tetra Tech, 2000), but the data are not sufficient to distinguish between loads from these two sub-basins. Therefore, the watershed sediment and water column loads from sub-basins 1 and 3 were assumed to have equal mercury concentrations to provide a rough partitioning of the load estimates. The resulting loads from individual sub-basins in the McPhee watershed are shown in Table 4-9.

Table 4-9 presents both gross loading estimates and estimates converted to an areal basis ($mg/km^2/yr$). Loading on a mass per unit area basis appears to be elevated in sub-basins 1, 2, 4, 10, and 11. These are the higher elevation sub-basins in the watershed and also are associated with mining activity. Mercury contamination may occur both as a direct result of mining where mercury is present in the ore deposits and is released from tailings or mine seeps, and through releases associated with gold amalgamation with mercury, a technique in common use through the 1930s.

The highest areal loading rate by far in the McPhee watershed is estimated for sub-basin 2, which is the Silver Creek drainage. The station at the outlet of this creek (MCP-11) had 4.25 ng/L total mercury in water in June 1999 but only 0.75 ng/L in August (see Tetra Tech, 2000 for sample results). On the other hand, sediment concentrations were 48 ng/g total mercury in June and 103 ng/g mercury in sediment in August 1999. Station MCP-12, in the middle reach of Silver Creek, below the Rico-Argentine mine tailings, also showed a strong difference between water samples, with 3.54 ng/L in June and 0.94 in August. Average concentration of total mercury in sediment was 48.3 ng/g. MCP-21, on upper Silver Creek, was sampled only in August and had 0.96 ng/L in water and 24.9 ng/g total mercury in sediment. Mercury concentrations thus appear to increase along the length of Silver Creek. In addition, Tetra Tech (2000) sampled a mine seep on Silver Creek (MCP-11B). This seep averaged 4.9 ng/L total mercury in water and 205 ng/g in sediment.

Within sub-basin 1 there are no mainstem samples, but several mine seeps were sampled: MCP-13 (mine seep at former sulfuric acid plant), MCP-14 (Horse Creek), and MCP-15 (upper mine seep on the Dolores River). Water concentrations in these seeps ranged from 1.5 to 21 ng/L in June and from 0.45 to 1.6 ng/L in August, while sediment concentrations ranged from 38 to 284 ng/g.

Sub-basins 1 and 2 intersect the Rico mining district, which has rich ore deposits first mined in 1879 for minerals, including gold. A large number of abandoned mines and several mine seeps are present. The ore in this district occurs primarily as sulfide replacement deposits, which are often associated with mercury. The Rico-Argentine mine on Silver Creek was one of the largest mines in the area and has previously been suggested as a source of mercury contamination (Tetra Tech, 2000).

On the West Dolores River (sub-basins 4 and 10), samples were collected at the mouth (MCP-3) and at an up-river location (MCP-4), as well as from a seep below Poor Boy Mine (MCP-10). All sediment concentrations reported are relatively unremarkable (less than 50 ng/g total mercury), but water column mercury concentrations were elevated, reaching as high as 5.62 ng/L total mercury in June sampling at MCP-4. Significant mining activity occurred in the West Dolores watershed, primarily on Cold Creek near Dunton, about 36 miles upstream of the Reservoir. The elevated water column concentrations at MCP-4 suggest there are likely unidentified mine seep sources in this watershed.

Within sub-basin 11 (Bear Creek), only an outlet station was sampled. Sediment concentrations were quite low, about 5 ng/g, but water column concentrations were elevated. Again, this may indicate loading to the water column from upstream mine seeps. The upper parts of Bear Creek are in the La Plata mining district, opened in 1873. Gold was mined in this district, and native mercury and mercury tellurides are present (Tetra Tech, 2000).

Loads by sub-basin for Narraguinnep Reservoir are shown in Table 4-10. The estimates for total watershed mercury mass loading are low relative to McPhee. While the estimates yield a high areal loading rate for sub-basin 1, the small size of this sub-basin results in a small total load.

Estimates of mercury loading in the interbasin transfer from McPhee to Narraguinnep are based on the median total mercury concentration in the water column observed in McPhee during 1999 sampling (1.65 ng/L). This median value is multiplied times the average amount of the diversion from McPhee to the Montezuma Valley Irrigation Company (MVIC) reported as going into storage on Annual Water Diversion Reports filed with the State Engineer over the period 1989-1989 (7,952 ac-ft per yr). Note that only a small portion of the total diversions through the Lone Pine Lateral (about 6 percent on average) goes into storage in Narraguinnep, with the remainder distributed directly through MVIC's canal system.

Table 4-8. Cumulative Upstream Mercury Loads at Nodes in the McPhee Watershed

Node	Sample Station	Sub-basins	Water Column Mercury Load (g/yr)	Sediment Mercury Load (g/yr)	Total Mercury Load (g/yr)	Total Mercury Areal Loading ($mg/km^2/yr$)	Areal Column (mg/k
2	MCP-11	2	49.5	37.4	86.9	4830.1	275
4	MCP-3	4,10	647.1	61.0	708.1	1626.7	148
5	MCP-5	1,2,3,5,11	1283.2	72.0	1355.2	1860.2	175
6	Median*	6,8	296.8	88.2	385.0	873.6	67
9	MCP-2	9	85.5	0.4	85.9	474.1	47
10	MCP-4	10	137.3	8.9	146.2	1352.5	127
11	MCP-7	11	140.3	0.5	140.8	1576.9	157
12	MCP-17	1,2,3,4,5,7,9, 10,11,12	2278.7	133.4	2412.1	1455.5	137

* No monitoring data are available for this watershed. Data from adjacent location were used to estimate mercury loadings.

Table 4-9. Individual Sub-basin Mercury Loads in the McPhee Watershed

Watershed	Sample Station	Water Column Mercury Load (g/yr)	Sediment Mercury Load (g/yr)	Total Mercury Load (g/yr)	Total Mercury Areal Loading ($mg/km^2/yr$)	Areal Column (mg/k
1	Difference[b]	349.2	10.4	359.6	1901.2	18
2	MCP-11	49.5	37.4	86.9	4835.8	27
3	Difference[b]	566.9	17	583.9	967.5	93
4	Difference[b]	509.8	52.1	561.9	1290.9	11
5	Median[a]	177.3	6.7	184.0	252.6	24
6	Median[a]	156.2	52.2	208.4	472.9	35
7	Difference[b]	172.4	0	172.4	131.8	13
8	Median[a]	140.6	36	176.6	957.9	76
9	MCP-2	85.5	0.4	85.9	474.1	47
10	MCP-4	137.3	8.9	146.2	1352.3	12
11	MCP-7	140.3	0.5	140.8	1576.7	15
12	Difference[b]	90.5	0	90.5	54.6	5
Total to Reservoir		**2575.5**	**221.6**	**2797.1**	**1333.2**	**12**

[a] No monitoring data are available for this watershed. The median of sample values was used to estimate mercury loadings.

[b] Watershed estimate obtained by differencing cumulative estimates in Table 4-8.

Table 4-10. Individual Sub-basin Mercury Loads in the Narraguinnep Watershed

Watershed	Sample Station	Water Column Mercury Load (g/yr)	Sediment Mercury Load (g/yr)	Total Mercury Load (g/yr)	Total Mercury Areal Loading ($mg/km^2/yr$)	Areal Column (mg/k
1	Nar-2	0.3	20.2	20.5	8877.5	121.6
2	Median[a]	0.2	0.9	1.1	604.5	120.7
3	Median[a]	1.4	1.5	2.9	239.2	112.1
4	Nar-1	0.2	0	0.3	111.7	99.5
5	Median[a]	0.4	0	0.4	170.5	169.8
6	Median[a]	0.3	0	0.3	136.5	120.7
Inflow from McPhee	MCP-A	15.9	0	15.9	0	0
Total to Reservoir[b]		**18.7**	**22.6**	**41.4**	**1109.9**	**118.8**

[a] No monitoring data are available for this watershed. The Median of sample values was used to estimate mercury loadings.

[b] Areal estimates include load from direct watershed only and exclude inflow from McPhee.

The watershed loading estimates of mercury loads transported in the water column and with scour and bedload of sediment may be combined with the estimates of direct atmospheric deposition of mercury to the lake surface presented in Section 3.3 to estimate total external mercury loads. Additional loading via storage in snowpack has not demonstrated to be a significant source at this time. The load estimates are summarized in Table 4-11. In addition to loading rates, this table also summarizes load per volume and surface area of the lakes, both of which are useful indices of potential biotic impact. Highest volumetric and areal loading rates are seen for Narraguinnep, followed by McPhee.

Table 4-11. Summary of Mercury Load Estimates for McPhee and Narraguinnep Reservoirs

Reservoir	Watershed Runoff (g/yr)	Watershed Sediment (g/yr)	Interbasin Transfer (g/yr)	Atmos. Deposition (g/yr)	Total (g/yr)	Load per Volume (mg/ac-ft)	Load per Surface Area (mg/m^2)
McPhee	2,576	222	0	251	3,049	4.66	0.098
Narra-guinnep	2.7	22.7	15.9	36.8	78.1	4.59	0.035

Table 4-12 re-expresses the loads on a percentage basis. Loading to McPhee appears to be dominated by water column loads derived from watershed runoff. This likely reflects the significance of mercury loading in dissolved and suspended form from mine seeps. Atmospheric deposition to the lake surface accounts for less than 10 percent of the total load to McPhee but close to 50 percent for Narraguinnep. Loads to Narraguinnep also include a significant contribution via interbasin transfer from McPhee.

Table 4-12. Mercury Load Source Percent Contributions for McPhee and Narraguinnep Reservoirs

Reservoir	Watershed Runoff	Watershed Sediment	Interbasin Transfer	Atmospheric Deposition
McPhee	84.5 %	7.3 %	0.0 %	8.2 %
Narraguinnep	3.4 %	29.1 %	20.4 %	47.1 %

4.5 Lake Hydrologic Model

The hydrologic behavior of the Reservoirs, particularly residence time, is an important factor in determining mercury response. Because the estimates of watershed loading are best interpreted as long-term averages, the hydrologic behavior of the Reservoirs was also represented on a long-term average basis by generating average monthly water balances.

For McPhee Reservoir, daily water balance accounting records were provided by the Bureau of Reclamation (John Simons, USBR Upper Colorado District, personal communication, January 11, 2000). These include estimates of inflow, releases, evaporation/seepage losses, and storage volume. Daily records of lake volume were first used to interpolate surface area and average depth, based on the Reservoir stage-storage-area curve. Data from October 1, 1986 (when the Reservoir first approached capacity) through September 30, 1999 were used to estimate average monthly behavior after deleting some apparently erroneous points. These results were smoothed slightly to provide closure on the annual balance. The average monthly water balance for McPhee Reservoir is summarized in Figure 4-9. In this figure, the "Releases to MVIC" represent the total diversions to the Montezuma Valley Irrigation Company (MVIC), not all of which actually reach Narraguinnep Reservoir.

Over the period shown, McPhee had an average depth of 81.5 feet, surface area of 3,890 acres, volume of 318,000 acre feet, and annual inflow of about 380,000 acre feet. This yields an average residence time of 0.82 years.

The water balance information available for Narraguinnep is much less detailed. The Colorado Division of Water Resources, Water Division 7, provided a stage-storage-area curve, daily records of transbasin diversions from McPhee, and monthly accounting of storage and releases for 1989 to 1999 (Kenneth A. Beegles, Division Engineer, personal communication to Kathryn Hernandez, USEPA Region 8, February 18, 2000). Over this period, the average annual release from Narraguinnep was 6,642 ac-ft. Depths and volumes appear to have been relatively stable (except during 1994) with an average depth of about 67.5 feet, volume of about 17,000 ac-ft, and surface area of 550 acres. This corresponds to a residence time of 2.5 years.

4.6 Lake Mercury Cycling and Bioaccumulation Model

Cycling and bioaccumulation of mercury within McPhee were simulated using the Dynamic Mercury Cycling Model (D-MCM; Tetra Tech, 1999c). D-MCM is a Windows 95/NT-based simulation model that predicts the cycling and fate of the major forms of mercury in lakes, including methylmercury, Hg(II), and elemental mercury. D-MCM is a time-dependent mechanistic model, designed to consider the most important physical, chemical, and biological factors affecting fish mercury concentrations in lakes. It can be used to develop and test hypotheses, scope field studies, improve understanding of cause/effect relationships, predict responses to changes in loading, and help design and evaluate mitigation options.

A schematic overview of the major processes in D-MCM is shown in Figure 4-10. These processes include inflows and outflows (surface and ground water), adsorption/desorption, particulate settling, resuspension and burial, atmospheric deposition, air/water gaseous exchange, industrial mercury sources, *in situ* transformations (e.g. methylation, demethylation, MeHg photodegradation, Hg(II) reduction), mercury kinetics in plankton, and bioenergetics related to methylmercury fluxes in fish.

Model compartments include the water column, sediments, and a food web consisting of three fish populations. Mercury concentrations in the atmosphere are input as boundary conditions to calculate fluxes across the air/water interface (gaseous exchange, wet deposition, dry deposition). Similarly, watershed loadings of Hg(II) and methylmercury are input directly as time-series data. The user provides for hydrologic inputs (surface and ground water flow rates) and associated mercury concentrations, which are combined to determine the watershed mercury loads.

The food web consists of six trophic levels (phytoplankton, zooplankton, benthos, non-piscivorus fish, omnivorous fish, and piscivorus fish). Fish mercury concentrations tend to increase with age and thus are followed in each year class. Bioenergetics equations for individual fish (Hewitt and Johnson, 1992) have been adapted to simulate year classes and entire populations.

The Electric Power Research Institute (EPRI) has funded development of the D-MCM model. It is an extension of previous mercury cycling models developed by Tetra Tech, including the original Macintosh-based MCM models developed during the EPRI-sponsored Mercury in Temperate Lakes Project in Wisconsin (Hudson et al., 1994) and the subsequent steady-state Regional Mercury Cycling Model (R-MCM) (Tetra Tech, 1996). The original model was developed for a set of seven oligotrophic Wisconsin seepage lakes. R-MCM has been applied to 21 lakes in Wisconsin; Lake Barco, Florida; and Lake 240 at the Experimental Lakes Area, Ontario. Performance of the model on the large data sets available for Wisconsin is summarized in Figure 4-11.

The present version of D-MCM has updated mercury kinetics and an enhanced bioenergetics treatment of the food web. The predictive capability of D-MCM is evolving but is currently limited by some scientific knowledge gaps, which include:

- The true rates and governing factors for methylation and Hg(II) reduction;
- Factors governing methylmercury uptake at the base of the food web; and
- The effects of anoxia and sulfur cycling.

For example, there is evidence that anoxia and sulfides can affect mercury cycling and influence water column mercury concentrations in lakes (e.g. Benoit et al., 1999; Driscoll et al., 1994; Gilmour et al., 1998; Watras et al., 1994), but the underlying mechanisms and controlling factors have not been quantified.

Another important assumption in the current version of D-MCM is that all of the Hg(II) on particles is readily exchangeable. This results in longer predicted response times for lakes to adjust to changing conditions or mercury loads than likely would occur. It is quite plausible that a significant fraction of Hg(II) on particles is strongly bound, reducing the pool size of Hg(II) available to participate in mercury cycling and the time required for fish mercury concentrations to adjust to changes in mercury loadings. The magnitude of this error potentially can be quite large for oligotrophic lakes with very low sedimentation rates and very long particulate Hg residence times in the surficial sediments. For systems that have very high sedimentation rates, such as is found in many reservoirs, the practical consequence of this assumption could be quite small. D-MCM modifications are planned to include both rapid and slow exchange of Hg(II) on particles. Experimental work is also proposed to develop the associated input values for the model.

4.7 D-MCM Model Application to McPhee Reservoir

4.7.1 Approach to Model Calibration

The model was initially calibrated on the basis of estimated long-term average conditions for McPhee Reservoir. Most of the site mercury data used for the calibration were collected by Tetra Tech, Inc. during field campaigns in June and August 1999 (Tetra Tech, 2000). Watershed loads for total mercury were estimated from a watershed model as described in Section 4.3. Estimates of atmospheric wet Hg(II) deposition are described in detail in Section 3.3. They are based primarily on 1999 mercury deposition data from Buffalo Pass, Colorado and a relationship to SO_4/NO_3 deposition in southwest Colorado monitored by NADP.

It should be noted that the estimated atmospheric deposition of mercury to McPhee Reservoir constitutes less than 10 percent of the total mercury load. As a result, the model calibration is not particularly sensitive to uncertainties in the estimated rate of atmospheric deposition.

The D-MCM model was calibrated to reproduce observed mercury concentrations in sediments, water and fish. An existing calibration for Little Rock Reference Lake in Wisconsin was used as a starting point that included previously calibrated values for all parameters relevant to mercury cycling (partitioning and reaction rate constants, etc.). Inputs associated with site conditions (bathymetry, flow rates, temperature, water chemistry, particulates, etc.) and external mercury loading were then modified to reflect conditions at McPhee Reservoir, where data were available or could be estimated. The model was then run and results compared to field data. In general, the calibration procedure is an iterative process but essentially follows, in sequence, the six steps below:

1. Calibration of model to match observed bulk sedimentation rates.

2. Calibration of growth rate and weight vs. length relationships for relevant fish species. Adjustment of population sizes to match lake or reservoir productivity.

3. Adjusting, if necessary, selected model constants so that the partitioning of Hg(II) and methylmercury concentrations between dissolved and particulate phases agrees with observations in both sediments and the water column.

4. Adjusting model parameters until methylmercury concentrations in water (unfiltered) and sediments (on solids) agree with observations. Again, calibration might involve adjusting partitioning of MeHg onto solids and in rare cases modifying rate constants for reactions such as methylation and demethylation.

5. Adjusting model parameters, if necessary, so that methylmercury concentrations in the lower food web agree with observations. Partitioning of MeHg into benthos and zooplankton can be adjusted.

6. Examining fish mercury levels. Diet and, in rare instances, species-specific bioenergetic parameters can be modified to improve agreement between the model and observed fish mercury levels.

It was assumed that the available data reasonably encompassed current mercury fluxes and concentrations at McPhee Reservoir and that these conditions were reasonably stable. There is some uncertainty in these assumptions, since long-term records are not available to confirm them, and temperate reservoirs are known to experience increased mercury concentrations in fish after flooding (Bodaly et al., 1997, Brouard et al, 1990, Canada-Manitoba Governments, 1987). The duration of this increase is still a matter of investigation but can last for more than a decade in sport fish at the top of the aquatic food web. The model was then run for simulations of 100 years with annual deposition patterns and site conditions repeating year after year, often with monthly frequencies for inputs. The resulting mercury concentrations and fluxes after the system had effectively stabilized (i.e., concentrations were not changing year to year) are reported on a weekly basis for the 101st year of the simulation to examine the seasonality of the predictions.

4.7.2 Approach to Developing an Hg(II) Dose- Fish Response Curve

One of the central questions for the McPhee Reservoir mercury TMDL modeling exercise was to predict the relationship between external Hg(II) loading and long-term fish mercury concentrations. A 15-inch (38.1 cm) smallmouth bass is the benchmark standard for the analyses, as described in Section 2. To make these predictions, we ran simulations with different Hg(II) loads maintained for a period of 100 years until fish mercury concentrations were at a quasi-steady state from year to year. Simulations focused on the potential effects of Hg(II) load reductions on fish mercury concentrations, with predictions made for load reductions of 15, 25, 50, and 60 percent of current estimates of total atmospheric Hg(II) deposition (wet and dry combined). These results were then combined in plots to show the shape of the Hg(II) dose-long-term fish Hg response curve. When running simulations with Hg(II) deposition rates other than current loadings, we had to make assumptions about other external mercury sources. For the simulations examining long-term predicted fish Hg concentrations for different loads, we adjusted atmospheric methylmercury deposition, inflowing methylmercury and inflowing Hg(II) concentrations in proportion to the reduction in atmospheric Hg(II) deposition.

4.7.3 Approach to Predicting the Timing of the System Response

To examine the time required for fish mercury concentrations to respond to load reductions, simulations were run for 100 years with Hg(II) deposition held constant at current estimated levels. The loads were then instantaneously reduced to a constant lower level. We examined the response dynamics of Hg levels in 15-inch smallmouth bass for load reductions of 15, 25, 50 and 60 percent from current atmospheric deposition rates to develop the response curve.

4.8 Lake Model Scenario Development

4.8.1 McPhee Reservoir Characteristics

General characteristics of McPhee Reservoir are summarized in Table 4-13. Additional information on characteristics of the Reservoir is available in Section 1 and in Tetra Tech (2000).

Table 4-13. McPhee Reservoir Characteristics

Parameter	Value
Year of Reservoir creation	1983-84 (filled by 1986)
Reservoir area at normal pool	1809 ha
Surface water depth (max)	82.36 m (corresponds to 2110.40 m elevation)
Water temperatures (monthly means)	~ 2 to 20 C
Mean annual water level fluctuation	Approx. 10 m
Productivity	Oligotrophic to mesotrophic
Flow pattern	Surface inflows, controlled outflows with diversion to Narraguinnep
Thermal stratification	Yes
Hydraulic residence time	~320 days

Anoxia	Not observed
Dissolved organic carbon	~ 3.9 mg L^{-1}
Surface water pH	~ 8.1
Surface water chloride	~ 3.9 mg L^{-1}
Surface water sulfate	435 *eq L^{-1}
Total suspended solids	~ 3.7 mg/L
Predatory fish	smallmouth bass and largemouth bass

4.8.2 Inputs for Model Simulations

Input data types and sources for simulations of McPhee Reservoir are summarized in Table 4-14. Additional details of the development of specific inputs are provided in the following sections, and information used to estimate hydrology is described in Section 4.3.

Reservoir Bathymetry and Water Levels

The relationship between reservoir depth and surface area was calculated using data obtained from a U.S. Bureau of Reclamation operational model of lake, described in Section 4.5. McPhee Reservoir experiences a mean annual water level fluctuation on the order of 10 m. The effects of water level fluctuations on fish mercury concentrations have been considered (Tetra Tech, 1995) but are not known. D-MCM, as a lake model, was not designed with the capability to model effects of large fluctuations in water level on mercury cycling. For the purposes of this study, we calibrated the model with a constant water level at a depth of 80.36 m at the deepest point in the Reservoir.

Two sediment zones were specified: an epilimnetic zone and a hypolimnetic zone. Sediments above the lowest level of annual migration of the thermocline were included in the epilimnetic zone. The active sediment layer thickness in both zones was assumed to be 3 cm.

Table 4-14. Summary of Lake Model Inputs for McPhee Reservoir by Major Data Type Category

Data Type	Parameter Estimate and Source
Hydrologic Data	
Precipitation	Monthly aggregation of daily data observed at Dolores (1980-99) (see Section 4.3)
Surface water elevations	Obtained from U.S. Bureau of Reclamation operational data for Reservoir
Surface flow	Smoothed average of U.S. Bureau of Reclamation data for Oct. 1986 (Reservoir first approaches full pool) to Sept. 1999
Physical Data	
Water and air temperature	Data estimated from daily air temperature values for Yellow Jacket COOP SOD station (see section 4.3)
Mercury Loadings	
Wet Hg(II) deposition	Estimated as described in Section 3.3
Dry Hg(II) deposition	Estimated using assumption that dry = 0.65 of wet deposition (see Section 3.3)
Upstream surface water concentrations – Hg(II)	Concentrations based on June and August 1999 data reported in Tetra Tech (2000) as processed in the watershed model (Section 4.3) to calculate long-term average flow-weighted concentrations using watershed simulation for 1980-1999 meteorology
Upstream surface water concentrations – MeHg (unfiltered)	Based on average of Dolores River data (June and August, 1999, sites NCP3, MCP5, MCP17), Tetra Tech (2000)
Surface Water Chemistry	
Dissolved Organic Carbon (DOC)	Mean value of field data from 6/99 and 8/99 (Tetra Tech, 2000)
pH and dissolved oxygen	Mean value of field data form 6/99 and 8/99
SO_4^{2-}	Mean value of field data from 6/99 and 8/99
Hg Concentrations in Reservoir	
Surface water Hg_{total} and MeHg (filtered and unfiltered)	Mean value of field data form 6/99 and 8/99
Sediment Hg	Mean value of field data form 6/99 and 8/99
Sediment porewater chemistry	No data available
Food Web	
Yellow perch Hg concentrations for model calibration	1999 sampling (see Section 1.5)
Smallmouth bass mercury concentrations for model calibration	1999 sampling (see Section 1.5). The data are contained in MCP899.xls (1/12001) and Tetra Tech, Inc. (2000)
Fish growth	No site data available. Used average growth rate of fish in the Central Front Range of Colorado (CO Fishing Federation, 1996)
Phytoplankton mercury	No data available
Zooplankton mercury	1999 sampling
Benthos mercury (Oligochaetes [red worms] and fly larvae)	August 1999 field data (Tetra Tech, 2000)

Water Temperature and Stratification

Mean monthly air temperature data were available from Yellow Jacket, Colorado, near McPhee, for the period 1980-1999 (Section 4.3). Continuous measurements of surface water temperatures for McPhee Reservoir were not available, although limited data were collected during the June 1999 and August 1999 sampling programs. Mean monthly surface water temperatures were therefore estimated on the basis of air temperatures from Yellow Jacket, with a lag time introduced (Figure 4-12).

Direct measurements of vertical temperature profiles are available from June and August 1999 (Tetra Tech, 2000), and indicate that thermal stratification does occur. The Reservoir was assumed to stratify in May and turn over in October. While ice does form on McPhee Reservoir, coverage is typically only partial, as the median air temperature in the coldest month (January) is only about -3 °C. The D-MCM model does not currently accommodate partial ice cover, and simulations assumed the site to be ice-free throughout the year.

External Mercury Loadings

The development of estimated atmospheric Hg(II) deposition is described in Section 3.3. Values used in simulations are shown in Figure 4-13. The development of estimated external loadings of total mercury from the watershed is described in Section 4.4. Values of estimated inflowing Hg(II) loads are shown in Figure 4-14.

No data were available for the direct atmospheric deposition of MeHg. Atmospheric deposition of MeHg is typically much smaller than that of Hg(II), and simulation results are not sensitive to MeHg atmospheric loading at these typically low levels. In lieu of local data, it was estimated that the annual load of MeHg to the Reservoir surface was 0.084 $\mu g\ m^{-2}\ yr^{-1}$. This was based on the use of a mean annual MeHg concentration similar to that estimated for northern Wisconsin (0.08 to 0.16 ng L^{-1} [Fitzgerald et al., 1994]), combined with the annual precipitation to McPhee Reservoir. Dry deposition rates for MeHg were assumed to be negligible.

Surface stream loading of methylmercury was estimated from data taken at MCP17, a station on the Dolores River at the inflow to McPhee Reservoir, for July and August of 1999. Methylmercury concentration at three downstream stations, MCP-17, MCP-3, and MCP-5, was similar and averaged 0.039 ng/L. Figure 4-15 shows the estimated monthly flux of MeHg in surface waters flowing into McPhee Reservoir. These fluxes were calculated assuming an MeHg concentration of 0.039 ng/L.

Water Chemistry Inputs

Several water quality parameters have been identified as having an impact on concentrations of total and methylmercury in freshwater systems. In particular, dissolved organic carbon, pH, and chloride have received much attention as factors influencing rates of mercury solubility, methylation, and demethylation. Table 4-13 shows the values used for these parameters during McPhee Reservoir simulations. Mean values were assigned and held constant during the simulations.

Food Web Inputs

The simplified food web in D-MCM is composed of six principal components, including phytoplankton, zooplankton, benthos, and the fish which are treated as three separate trophic levels (non-piscivores, omnivores, and piscivores).

Smallmouth bass and yellow perch were chosen to represent the piscivore and omnivore fish species respectively. The non-piscivore can be considered a generic species that is a composite of all small prey fish species in the Reservoir.

No detailed studies have been conducted on feeding preferences of fish within McPhee Reservoir. Estimated feeding patterns were provided by Mike Japhet, the CDOW biologist assigned to McPhee Reservoir (personal communication to John Radde, Tetra Tech). Non-piscivores were assumed to consume only plankton and benthic organisms. Yellow perch were assumed to initially eat plankton and benthos and then increase the fraction of fish in their diet as they grew. Smallmouth bass were assumed to follow a dietary trend similar to that of perch but ultimately consumed a larger fraction of fish than did the perch. Dietary preferences, by cohort for the three fish species included in the final calibration are provided in Tables 4-15 through 4-17 and Figure 4-16.

Table 4-15. Dietary Preferences of Composite Non-Piscivore Population Used for Final Calibration

Dietary Item	Fraction of diet by weight for non-piscivorous fish (all ages)
Phytoplankton	0.1
Zooplankton	0.4
Benthos	0.5

Table 4-16. Dietary Preferences of Yellow Perch Used for Final Calibration

	Fraction of diet by weight for yellow perch by age range			
Dietary Item	**0-1**	**1-2**	**2-3**	**>3**
Zooplankton	0.3	0.2	0.25	0.2
Benthos	0.7	0.7	0.50	0.5
Fish	0	0.1	0.25	0.3

Table 4-17. Dietary Preferences of Smallmouth Bass Used for Final Calibration

	Fraction of diet by weight for smallmouth bass by age range			
Dietary Item	**0-1**	**1-2**	**2-3**	**>3**
Zooplankton	0.45	0.15	0	0

Benthos	0.55	0.60	0.75	0.5
Fish	0	0.25	0.25	0.5

The relationship between fish length and weight is also important in D-MCM because there is a preferred prey size range for piscivory, based on fish lengths. Furthermore, the relationship between length and weight is needed to predict fish methylmercury levels by length. The calibrated weight versus length relationships for perch and smallmouth bass are shown together with observations from June and August 1999 in Figures 4-17 and 4-18.

Fish growth rates can significantly affect their mercury body burdens. Figures 4-19 and 4-20 show calibrated growth rates for yellow perch and smallmouth bass. No site-specific growth rate data were available. Yellow perch growth was calibrated to data from 55 Wisconsin lakes (Snow and Sand, 1992). Smallmouth bass growth was calibrated to growth rates reported for Central Front Range Reservoirs of Colorado (Colorado Fishing Federation, 1996).

Particle Dynamics

There were no site-specific data available for particle settling or bulk sedimentation rates for McPhee Reservoir. Limited data for total suspended solids in the water column were available however (Table 4-14). These particles were assigned a settling velocity within the range used for other lake simulations with D-MCM, to generate a supply of particles to the sediments. Sediment decomposition rates in the model depend on assigned particulate turnover rates and particle carbon fractions. These inputs were also estimated based on previous D-MCM lake studies. Particle resuspension rates were assumed of secondary importance. With the above information, the model solved for bulk sedimentation (long-term burial) rates. The calibrated particle fluxes for epilimnetic and hypolimnetic sediments are shown in Figures 4-21 and 4-22.

4.9 McPhee Reservoir Simulation Results

4.9.1 D-MCM Calibration to Current Loadings, McPhee Reservoir

Good agreement between model predictions and observed mercury levels in sediments and surface waters were achieved using the original parameters from calibration of the model to 21 Wisconsin seepage lakes. Model predictions for McPhee Reservoir are presented together with observed concentrations for Hg(II) and methylmercury in surface waters and sediments in Table 4-18 (above). Model predictions fell within the range of observed values for both unfiltered and dissolved total mercury in surface waters (Figure 4-23) and for particulate total mercury in the sediments (Figure 4-24).

The calibrated simulation did produce low methylmercury levels characteristic of those found in McPhee Reservoir surface waters (Figure 4-25). Predicted methylmercury concentrations in sediments were slightly higher than observations, but still low (Table 4-18).

Table 4-18. Comparison of Observed and Predicted Hg Concentrations in Surface Waters and Sediments in McPhee Reservoir

Parameter	Units	Predicted		Observed	
		Mean	Range	Mean	Range
Unfiltered total Hg, surface water	ng/L	1.56	1.24 to 2.58	1.61 (n=9)	0.87 to 2.46
Unfiltered MeHg, surface water	ng/L	0.029	0.020 to 0.051	0.026 (n=9)	0.012 to 0.045
Total Hg, sediment solids	ug/g dry	0.053	0.052 to 0.055	0.049 (n=10)	0.023 to 0.131
MeHg, sediment solids	ug/g dry	0.00052	0.0003 to 0.0006	0.0002 2 (n=9)	0.00002 to 0.0006

The model initially was not able to account for the observed levels of MeHg in yellow perch and smallmouth bass, consistently underpredicting mercury levels in these fish. This was not unexpected in view of the low methylmercury concentrations in surface waters and sediments and the resulting low predicted concentrations in benthic organisms. The model constant for partitioning of methylmercury into benthic organisms was increased from 40 to 60 (dimensionless) to produce better agreement between predicted and observed yellow perch methylmercury levels (Figure 4-26).

The 50 percent increase in benthic methylmercury partitioning during calibration is not considered excessive given the level of uncertainty associated with this parameter. Field data at McPhee Reservoir for sediment methylmercury concentrations are limited (mean 0.00022 µg/g dry weight, n=9) and there are few benthic methylmercury data available (mean less than 10 ng/g, n=3). While these data were not all colocated, the resulting mean partitioning value would be approximately 45. The value of 60 was needed to improve model predictions for mercury concentrations in yellow perch. After modifying the partitioning constant the resulting predicted concentrations of methylmercury in benthos (30 -35 ng g^{-1} wet) are still within the range reported for a variety of benthic organisms in freshwater systems. Benthos are likely an important methylmercury source for fish and will require additional attention in future lake and reservoir studies.

The model still underpredicted smallmouth bass mercury levels after modification of the benthic partitioning parameter. This was addressed through the activity coefficient. The activity coefficient, ACT, is a fish activity multiplier from the Wisconsin Fish Bioenergetic Model that is influenced by a large number of environmental and physiological factors. ACT is meant to account for energy requirements for activity above and beyond routine metabolism, e.g. spent searching for food.

The ACT was initially set at a default value of 2.0 (Hewett and Johnson, 1992). During calibration ACT was increased from 2.0 to 5.60, which produced a very close agreement between observed and predicted smallmouth bass methylmercury. The required increase in ACT is a large one, but is necessary to reconcile the model with observations. As discussed in Section 4.10.1, the discrepancy between low methylmercury concentrations observed in water and sediments versus the more significant levels in smallmouth bass suggests a need for further field studies to refine the modeling. In particular, the modeling effort suggests that there may be prey items in the fish diet that had higher methylmercury concentrations than those sampled in the field. These could represent either species not sampled or elevated concentrations at localized areas not occupied during the sampling.

Figure 4-27 shows the improvement in fit obtained with the increased ACT value of 5.0.

4.9.2 Long-Term Hg(II) Deposition - Fish Hg Response Curve

A fundamental question to examine in this TMDL study was the relationship between external Hg(II) loading and long-term fish mercury concentrations. Once the model was calibrated to the current Hg(II) load estimates, simulations were carried out with loading reduced by 15, 25, 50, and 60 percent of current levels.

Figure 4-28 shows the predicted long-term MeHg concentrations in 15-inch smallmouth bass as a function of the fraction of the estimated current atmospheric loading. The predicted relationship between loading and fish mercury is nearly linear, although specific to this waterbody. A linear regression was performed on the long term predictions for 15-inch smallmouth bass mercury. The results are also provided in Figure 4-28. Interpolation using the regression line predicts that a reduction of 15 percent in atmospheric loading would produce the target long-term methylmercury levels of 0.5 μg/g in 15-inch smallmouth bass.

4.9.3 Dynamic Response of MeHg Levels in Smallmouth Bass

A second fundamental purpose for this TMDL modeling effort was to examine the temporal response of mercury levels in McPhee Reservoir smallmouth bass to reductions in external mercury loading. To address this issue simulations were first run for 200 years with current mercury loading levels in order to achieve quasi-steady state. At 200 years all external mercury loads associated with atmospheric deposition and inflows of total and methylmercury were reduced by the specified fraction and the simulation was then run for an additional 200 years under conditions of reduced external loading. It is recognized that there may be some lag time in the response of the catchment to reduced atmospheric deposition. The assumption that catchment loading responds instantaneously may lead to the prediction of a somewhat more rapid overall system response than may actually be the case.

The dynamic response of the methylmercury concentration in smallmouth bass to load reductions of 15, 25, 52 and 60 percent is presented in Figure 4-29. In all cases, methylmercury concentrations achieved a quasi-steady state predicted level within 25-30 years. A concentration of 0.5 μg/g is predicted to be achieved in under 20 years with a 15 percent reduction in loads. Furthermore, the long-term mercury level obtained with the dynamic 15 percent load reduction simulation agrees with the prediction based on the long-term Hg(II) deposition-fish Hg response analysis in Section 4.9.2.

Figure 4-30 shows the approach to steady state with a sustained load reduction represented as a fraction of the of the total change in concentration. The curves for the different load reduction scenarios are indistinguishable. This suggests that the rate at which fish mercury concentrations approached a new steady-state situation following a load reduction is independent of the magnitude of the load change. For example, 50 percent of the ultimate response in fish Hg was predicted to be achieved in approximately 6 years for all load reduction scenarios tested.

4.9.4 Fluxes of Hg(II) and Methylmercury for McPhee Reservoir

The predicted dominant source of mercury to McPhee Reservoir is inflow from the watershed, which provides 92 percent of total mercury and 87 percent of Hg(II) load to the Reservoir on an annual basis (Figure 4-31). Atmospheric deposition was predicted to contribute the remaining 8 percent of the annual total mercury supply (13 percent of the annual Hg(II) supply). The predicted importance of various loss pathways for inorganic mercury (Hg(II) or elemental Hg) is shown in Figure 4-32. Outflow is predicted to be the dominant removal mechanism for inorganic Hg (55 percent), with burial also significant (34 percent) and evasion a secondary loss mechanism for inorganic Hg (11 percent).

The dominant predicted source for methylmercury to McPhee Reservoir is also inflow (71 percent of total MeHg load to the Reservoir; see Figure 4-33). Internal production of methylmercury in sediments was predicted to contribute 15 percent of the annual MeHg supply and atmospheric deposition another 9 percent. Gas exchange with the atmosphere is predicted to contribute 7 percent of the annual MeHg supply to the Reservoir. This number is quite uncertain, however, given the lack of any data on atmospheric gaseous methylmercury concentration.

4.10 Discussion of McPhee Reservoir Results

4.10.1 Predicted Mercury Concentrations

D-MCM reasonably predicted concentrations of total and methylmercury in surface waters and sediments (Table 4-18; Figures 4-23 through 4-25). Total mercury concentrations in the surface waters and sediments of McPhee Reservoir are within the typical range for freshwater systems, with sediment concentrations being somewhat at the low end of the range. Methylmercury concentrations in surface waters and sediments (1999 observations and in the model) are also within the range typically seen in freshwater systems, although at the low end of the range. This suggests that if there was an increase in methylmercury levels following the creation of the Reservoir in the mid 1980s, this reservoir effect is no longer producing elevated MeHg concentrations in surface waters or sediments, at least in the areas sampled.

Mercury concentrations in yellow perch and smallmouth bass were initially underpredicted by the model, reflecting the low methylmercury concentrations predicted in surface waters, sediments, and the lower food web (plankton and benthos). Observed methylmercury concentrations in benthic organisms (oligochaetes (red worms) and fly larvae) were less than 10 ng g^{-1} wet weight when sampled in August 1999. These concentrations were incapable of supporting the mercury concentrations observed in fish. To reflect observed mercury concentrations in yellow perch with the model, concentrations in a significant portion of the perch diet needed to be on the order of 30-35 ng g^{-1} wet weight. This was achieved in the calibration by adjusting partitioning values for methylmercury between benthos and sediments from 40 to 60, which resulted in better predictions of methylmercury levels in yellow perch (Figure 4-26).

Once yellow perch mercury concentrations were calibrated, the model was still under-predicting observed mercury levels in smallmouth bass. To generate better model predictions it was necessary to adjust (1) the bass diet, (2) the mercury concentrations in the bass diet, or (3) parameters affecting the amount of food consumed. We adjusted a coefficient related to the food consumption required for activity spent searching for food (ACT), but it is equally plausible that the bass could be eating dietary items with higher concentrations than were observed in 1999 in the field or predicted by the model. Once these calibration adjustments were made, the model reasonably predicted MeHg levels in smallmouth bass.

Overall, the basic discrepancy between low methylmercury concentrations observed (and modeled) in water and sediments, versus the more significant levels seen in fish, particularly smallmouth bass would require further field studies to assess likely explanations. The modeling effort suggests there are probably dietary items eaten by perch and bass that have higher methylmercury concentrations than those sampled during field programs. It is also possible that while the model assumes homogeneous conditions within each sediment zone, there could be localized areas, not sampled, with increased sediment methylmercury production and higher benthic methylmercury concentrations than the model predicted.

4.10.2 Predicted Response of McPhee Reservoir to Changes in Hg Loading

Figure 4-28 indicates that in the longer term, fish mercury concentrations in McPhee Reservoir are predicted to respond significantly to changes in atmospheric Hg(II) deposition. A nearly linear relationship between atmospheric Hg(II) deposition and fish mercury concentrations is predicted, but the slope is not 1.0.

Figures 4-29 and 4-30 show that mercury concentrations in 15-inch smallmouth bass in McPhee Reservoir are predicted to respond significantly within the first decade following Hg loading reductions. Regardless of the magnitude of the load reduction, fish mercury concentrations are predicted to change by 50 percent of the ultimate response within 6 years. Within 25 years, 90 percent of the ultimate predicted response has occurred. The actual magnitude of the change in fish Hg is of course dependent on the magnitude of the load reduction, as shown in Figure 4-29. These results are significantly influenced by the assumption that concentrations of Hg(II) and methylmercury in inflows would drop immediately in proportion to reduced atmospheric deposition. If a lag time is in fact involved between reduced atmospheric Hg deposition and Hg concentrations in inflows, the response time for fish in McPhee Reservoir would be slower. This situation is quite plausible.

The predicted magnitude and timing of the response of fish mercury concentrations to changes in atmospheric Hg(II) deposition and concentrations (i.e., linear but with a non-zero intercept) is governed by, and to some extent uncertain, as a result of our current understanding of mercury cycling and the resulting assumptions in the model. Specifically, the following assumptions had a significant impact on the shape of the long-term dose-response curve and the timing of the response:

- Inflowing methylmercury and Hg(II) loads and atmospheric MeHg deposition were assumed to be reduced by the same percentage as Hg(II) deposition in scenarios with load reductions. This assumption is particularly important given that inflow is predicted to be an important, if not primary, source of Hg(II) and methylmercury to McPhee Reservoir.

- In-situ methylation occurs primarily in the sediments.

- Methylation depends on a bioavailable fraction of porewater Hg(II).

- Porewater Hg(II) concentrations are not currently at saturation. For example, it is plausible that additional Hg(II) loading could result in precipitation of the excess Hg(II) as cinnabar, and no change in porewater Hg(II). The model does not simulate cinnabar formation in any of the loading scenarios examined in the calibration.

Thus, the predicted response of fish Hg to load reductions in this study reflects the current level of understanding. This level of understanding is currently inadequate, however, to place a robust confidence in the predictions. The validity of the above assumptions needs resolution.

Finally, there is uncertainty associated with this modeling assessment because a sampling program on two dates in a single year (June and August 1999) cannot incorporate the natural variability of mercury concentrations and fluxes both seasonally and from year to year. The same limitation exists due to the lack of a long-term monitoring dataset for atmospheric mercury deposition at or near the site.

4.11 Mercury Responses in Narraguinnep Reservoir

There were neither sufficient hydrologic data nor available resources to complete a detailed lake model application for Narraguinnep Reservoir at this time. Narraguinnep, however, is predominantly supplied by diverted water from McPhee Reservoir and is physically near McPhee, experiencing the same climate forcing and areal atmospheric mercury loading. General mercury dynamics in Narraguinnep are expected to be similar to those in McPhee. The specifics of mercury dynamics in Narraguinnep are, however, expected to differ from McPhee due to a number of factors, including different residence time, different fish populations, and probable significance of methylation of mercury in wetlands surrounding the lake (which are in part fed by irrigation water diverted from McPhee).

The key assumption made for analysis of mercury responses in Narraguinnep is that, over the long term, fish body burdens will respond approximately linearly to reductions in external mercury load, as is predicted for McPhee. In fact, the responses predicted by D-MCM are always slightly nonlinear, with the rate of reduction in fish tissue being somewhat less than the rate of reduction in external loads. The reason for this offset is that the model contains some sources of mercury load that are not subject to reduction in the model scenarios. For McPhee, the major source of this un-reduced load is the exchange of gaseous methylmercury with the atmosphere. Internal production of methylmercury in the lake sediments (as opposed to wetlands) is believed to be of relatively low importance in McPhee, and is also assumed to be of relatively low importance in Narraguinnep. Given similar water column mercury concentrations in McPhee and Narraguinnep, and assumed nearly identical atmospheric conditions, the slope of the fish mercury response curve to external loading should be similar in Narraguinnep and McPhee.

The analysis for Narraguinnep was therefore developed through an empirical analogy to the detailed modeling work for McPhee, while accounting for the different biological characteristics of the two lakes. As discussed in Chapter 2, the target species for Narraguinnep is an 18-inch walleye. The analysis was then developed using the following steps:

1. The walleye data for Narraguinnep (Tetra Tech, 2000) were analyzed based on a log-log regression of fish mercury versus length. This yielded an estimated best estimate of current mercury tissue concentrations in 18-inch walleye of 0.93 µg/g wet weight (Figure 4-34).

2. The D-MCM modeled relationships from McPhee were used to predict the fractional reduction in long-term fish tissue concentrations of mercury as a function of reductions in external mercury loading.

The regression relationship from the D-MCM application to McPhee is $y = 0.9298 \cdot x + 0.0702$, where y is the fraction of current mercury in top-predator fish and x is the fraction of current external mercury loading. This relationship was developed for 15-inch smallmouth bass in McPhee, but the model simulation results in McPhee show that the predicted effects of load reductions on long-term fish mercury levels are similar across fish species and/or sizes. Thus, in the long-term, this relationship should also be appropriate for walleye in Narraguinnep.

The lack of a detailed, site-specific model does introduce additional uncertainty into the analysis of fish response in Narraguinnep Reservoir. This uncertainty could be reduced through the development and calibration of a detailed lake response model for Narraguinnep. Without such a model it is clear that significant reductions in mercury loading are needed to achieve water quality standards in Narraguinnep, but the estimated level of needed reductions is less certain than it would be with creation of a model. For both McPhee and Narraguinnep, collection of additional data over additional seasons and for additional physical and biotic compartments would improve both understanding of mercury dynamics and the accuracy of modeling. It is recommended that ongoing data collection be pursued, together with creation of a model for Narraguinnep, concurrent with efforts to reduce loads. This would enable adaptive fine-tuning of

TMDL load allocations over the course of the several decades estimated to be required to attain the full response of fish tissue mercury levels to changes in mercury loads.

5. TMDL, Load Allocations, and Wasteload Allocations

The linkage analysis provides the quantitative basis for determining the loading capacity of McPhee and Narraguinnep Reservoirs. This in turn allows estimation of the Total Maximum Daily Load (TMDL) and allocation of that load to point sources (wasteload allocations) and nonpoint sources (load allocations). The TMDL must also contain a Margin of Safety, which is described in detail in Section 6.2.

The final TMDL and corresponding allocations will be developed by the State of Colorado. This technical support document proposes a draft TMDL and allocations for demonstration purposes. Various alternative combinations of allocations could also be developed to meet water quality objectives.

5.1 Determination of Loading Capacity

A waterbody's loading capacity represents the maximum rate of loading of a pollutant that can be assimilated without violating water quality standards (40 CFR 130.2(f)). Application of the D-MCM lake mercury model provides best estimates of the loading capacity for mercury of McPhee Reservoir of 2,592 grams total mercury per year. This is the maximum rate of loading consistent with meeting the numeric target of 0.5 mg/kg mercury in fish tissue. The loading capacity estimate for Narraguinnep Reservoir is 39.1 grams total mercury per year.

This estimate of loading capacity is subject to considerable uncertainty, as described in the preceding sections. Uncertainty in the estimation of the loading capacity, and thus the TMDL, is addressed through the assignment of a Margin of Safety (Section 6.2).

It should also be noted that the loading capacity is not necessarily a fixed number. The numeric target for the TMDL is expressed as a mercury concentration in fish tissue. This numeric target is linked to external mercury load through a complex series of processes, including methylation/ demethylation of mercury and burial of mercury in lake sediments. Any alterations in rates of methylation or in rates of mercury loss to deep sediments will change the relationship between external mercury load and fish tissue concentration and would thus result in a change in the loading capacity for external mercury loads.

5.2 Total Maximum Daily Load

The TMDL represents the sum of all individual allocations of portions of the waterbody's loading capacity. Allocations are made to all point sources (wasteload allocations) and nonpoint sources or natural background (load allocations) The TMDL (sum of allocations) must be less than or equal to the loading capacity; it is equal to the loading capacity only if the entire loading capacity is allocated. In many cases it is appropriate to hold in reserve a portion of the loading capacity to provide a Margin of Safety, as provided for in the TMDL regulation.

Knowledge of mercury sources and the linkage between mercury sources and fish tissue concentrations in McPhee and Narraguinnep Reservoirs is currently subject to many uncertainties. (These uncertainties are discussed in more detail in Section 6.1). Accordingly, it is appropriate to allocate only a portion of the estimated loading capacity. Based on the analysis in Sections 5.4 and 6, an allocation of 70 percent of the loading capacity is proposed for this example. The Total Maximum Daily Load calculated for McPhee Reservoir would then be equivalent to a total annual mercury loading rate of 1,814 g/yr (70 percent of the loading capacity of 2,592 g/yr), while the TMDL for Narraguinnep Reservoir would be equivalent to a total annual mercury loading rate of 27.3 g/yr.

5.3 Unallocated Reserve

In this example, thirty percent of the estimated loading capacity is not allocated. Therefore, there is an estimated unallocated reserve of 778 g-Hg/yr in McPhee and 11.8 g-Hg/yr in Narraguinnep. The best estimate of uncertainty in the loading capacity analysis is that the true loading capacity lies within plus or minus 25 percent of the best estimate of annual loading (Section 6.1). The unallocated reserve is thus greater than the estimated Margin of Safety for the TMDL.

5.4 Load Allocations

Load allocations represent assignment of a portion of the TMDL to nonpoint sources. These allocations must be made even where there is considerable uncertainty about nonpoint loading rates. Federal regulations (40 CFR 130.2(g)) define a load allocation as follows:

> The portion of a receiving water's loading capacity that is attributed either to one of its existing or future nonpoint sources of pollution or to natural background sources. Load allocations are best estimates of the loading, which may range from reasonably accurate estimates to gross allotments, depending on the availability of data and appropriate techniques for predicting loading. Wherever possible, natural and nonpoint source loads should be distinguished.

The current state of knowledge of mercury sources in the watershed and transport to the lakes requires use of a "gross allotment" approach to the watershed as a whole, rather than assigning individual load allocations to specific tracts or land areas within the watershed. Loading from geologic sources has also not been separated from the net impacts of atmospheric deposition onto the watershed. Information is currently available to separate sources for load allocations to McPhee as follows:

- Direct atmospheric deposition onto the lake surface.
- Loading from the Rico/Silver Creek mining area.
- Loading from the Dunton mining area.
- Loading from the La Plata mining area.

- Generalized background watershed loading, including mercury derived from parent rock and soil material, residual mercury from mining operations other than those addressed above, and the net contribution of atmospheric deposition onto the watershed land surface.

For Narraguinnep, one important source of mercury load is inter-basin transfer from McPhee. This means that the allocations for McPhee might also need to be limited to meet targets in Narraguinnep. The following load allocations are considered for Narraguinnep:

- Direct atmospheric deposition onto the lake surface.
- Inter-basin transfer from McPhee Reservoir.
- Generalized background watershed loading, including the net contribution of atmospheric deposition onto the watershed land surface.

Direct Atmospheric Deposition

Direct deposition to the surface of McPhee Reservoir is estimated to provide about 251 g-Hg/yr (Table 3-3). This amount equals less than 10 percent of the estimated total annual mercury loading to the lake (Table 4-12). The atmospheric load to Narraguinnep is estimated at 37 g-Hg/yr, or about 47 percent of the total load. Atmospheric deposition of mercury to these Reservoirs is believed to derive from mercury sources, such as power plants and smelters, located throughout the Southwest. The influence of an individual source is related to the source's mercury emission rate, the form in which mercury is emitted, the source's proximity to the receptor, and atmospheric transport patterns (meteorology). As discussed in Section 3.3, areal atmospheric loading rates of total mercury at these lakes appear to be elevated above regional background, suggesting that a significant, but undetermined, portion of the atmospheric deposition load may be due downwind anthropogenic sources.

Narraguinnep and McPhee Reservoirs are close to one another and receive approximately the same areal rate of mercury deposition. Fish tissue concentrations in Narraguinnep, however, are much more strongly driven by atmospheric deposition than are fish tissue concentrations in McPhee. Therefore, the need for reductions in direct atmospheric deposition is driven by the goal of meeting fish tissue concentrations in Narraguinnep. A 75 percent reduction in atmospheric deposition loads to both Reservoirs is proposed in this example. This would leave a direct deposition load of 62.8 g-Hg/yr to McPhee and 9.5 g-Hg/yr to Narraguinnep.

Alternatively, a smaller reduction in atmospheric loading could be coupled with a larger reduction in watershed loading to meet the fish tissue concentration goals. It is likely that standards could be met in McPhee Reservoir solely through reductions in watershed loads. If the estimates developed in this report are correct, however, the needed reduction in loads for Narraguinnep (reduction of 51 g-Hg/yr) is greater than the existing load from the watershed and via inter-basin transfer (41 g-Hg/yr). It therefore appears that some degree of reduction in atmospheric loads (at least 25 percent, even if all other sources were eliminated according to the estimates presented in this report) will be needed to meet water quality objectives in Narraguinnep.

At this time, there are not sufficient data to allocate the atmospheric deposition component to individual sources. This will require further study, including both validation of the estimated atmospheric deposition rates and attribution of a portion of this load to specific stationary sources. It is anticipated that the proposed 75 percent reduction in atmospheric load might be achieved in part through reduced emissions at the major coal-fired power plants located within several hundred miles of the Reservoir; however, a portion of the net reduction might be obtained through reduction in the long-range background due to increased emissions controls on mercury in the United States and elsewhere. These issues will need to be resolved before full implementation of the TMDL is feasible. If emissions are reduced at the coal-fired power plants, continued monitoring (and adaptive management, as appropriate) should be pursued to monitor the mercury status in the Reservoirs - particularly at Narraguinnep, which is expected to respond more strongly than McPhee to changes in atmospheric loading of mercury.

Mining Areas

The analysis of areal loading rates of mercury in the McPhee watershed (Table 4-9) shows three areas where loading, on per-acre basis, is elevated. These areas are associated with the three historic mining districts in the watershed (Rico/Silver Creek, Dunton, and La Plata), and constitute model sub-basins 1, 2, and 3 (Rico); 4 and 10 (Dunton); and 11 (La Plata). Loading from these sub-basins is elevated due to a combination of input from mine tailings and mine drainage, plus naturally elevated background levels due to the presence of mercury-bearing sulfide ores. Estimated annual average mercury loads from these three areas amount to 1,879 g/yr. This constitutes 67 percent of the watershed mercury load and 62 percent of the total mercury load in the McPhee basin.

Sufficient data are not available at this time to determine allocations for individual mining sources. Indeed, it does not appear to be the case that there are a small number of dominant sources. For instance, the Rico-Argentine mine on Silver Creek has been identified as a significant source of mercury load, but the entire Silver Creek basin (sub-basin 2) appears to contribute only about 3 percent of the total watershed mercury load to McPhee Reservoir.

Although there do not appear to be single dominant sources, load from the mining district sub-basins constitutes the bulk of the mercury load in the watershed. Reductions in load to attain standards would likely need to rely on reductions from the numerous sources in these areas. The estimated needed reduction in loads from the mining areas is 50.8 percent, conditional on the proposed reduction in direct atmospheric deposition load cited above.

No known mining areas contribute mercury directly to Narraguinnep Reservoir; however, reduction in loads from mining sources to McPhee will also reduce the inter-basin transfer load to Narraguinnep.

Interbasin Transfer

The amount of mercury transferred from McPhee to Narraguinnep is dependent on the water column mercury concentrations within McPhee. The lake modeling suggests that, over the long term, these concentrations will decrease on an approximately one-to-one basis as external loads to McPhee decrease. Therefore, the reduction in inter-basin transfer load from McPhee to

Narraguinnep is assumed to be equal to the total decrease in mercury loading to McPhee needed to meet fish consumption guidelines in McPhee. This amounts to a 40.5 percent reduction. This report has not considered reductions in the volume of water supplied from McPhee to Narraguinnep or reductions in the mercury load within the inter-basin transfers (beyond the reduction in ambient concentrations in McPhee) as viable management options.

Background Watershed Loading to McPhee
Background loading from the non-mining areas of the watershed draining to McPhee Reservoir (areas other than sub-basins 1-4, 10, and 11) is estimated to contribute 919 g-Hg/yr. This mercury arises from apparently diffuse geologic sources, storage in stream beds, and atmospheric deposition onto the watershed. The diffuse watershed background will be difficult to control, given the large contributing area. Some reduction in background loading is expected if reductions in atmospheric deposition onto the watershed are achieved. It has not been possible to quantify the extent of these reductions at this time. Indeed, the complex exchange processes between soil and atmosphere may result in a very slow response to changes in atmospheric loading. USEPA (1997, pp. 2-11) notes: "Even if anthropogenic emissions were to stop entirely, leaching of mercury from soil would not be expected to diminish for many years." As a result of these uncertainties, a nominal 10 percent reduction in the existing background watershed loads from non-mining areas in the McPhee watershed is proposed.

Background Watershed Loading to Narraguinnep
Even with a 75 percent reduction in atmospheric loads, further reductions in net mercury loading to Narraguinnep appear to be needed to meet the TMDL. This additional reduction is assigned to the direct watershed loading to Narraguinnep. It is estimated that a 66 percent reduction in the background watershed loading (from 25.4 to 8.6 g-Hg/yr) will be needed in combination with the atmospheric load reduction to meet the fish tissue target in Narraguinnep. Background loads to Narraguinnep may be easier to address than background loads in the McPhee watershed, due to the small size of the direct drainage area. In addition, a significant part of the watershed mercury load to Narraguinnep may actually be attributable to mercury in irrigation water diverted through the Lone Pine lateral to agricultural land in the basin. Thus, reductions in the mercury concentrations in inter-basin transfer from McPhee to Narraguinnep may also help to reduce the background watershed load to Narraguinnep.

5.5 Wasteload Allocations

Wasteload allocations constitute an assignment of a portion of the TMDL to permitted point sources. There are no permitted point source discharges within the Narraguinnep watershed. Two small point sources within the McPhee watershed do not have mercury limits and are not believed to contribute significant amounts of mercury (see Section 3.1). Therefore, no wasteload allocations are included in the TMDL.

5.6 Allocation Summary

Example allocations for the McPhee and Narraguinnep mercury TMDLs are summarized in Tables 5-1 and 5-2. These allocations, based on best currently available information, are predicted to result in attainment of acceptable fish tissue concentrations within a time horizon of approximately 20 years. A delay in achieving standards is unavoidable because time will be required for mercury to cycle through the lake and food chain after loads are reduced.

It should be emphasized that these are potential, rather than final allocations. A key issue is the balance of allocations between watershed sources (including mining sources) and atmospheric sources. A much larger reduction in atmospheric loading as compared to watershed loading appears to be needed to achieve goals in Narraguinnep than in McPhee Reservoir, and addressing the mercury problems in McPhee alone could rely more on watershed controls than on atmospheric controls (see further discussion in Chapter 6). No cost-effectiveness analysis of potential allocations has been conducted at this time.

Table 5-1. Summary of Example TMDL Allocations and Needed Load Reductions (in g-Hg/yr) for McPhee Reservoir

Source	Allocation	Existing Load	Needed Reduction
Wasteload Allocations	0	~0	~0
Load Allocations			
Atmospheric Deposition	63	251	188
Rico/Silver Creek Mining Area	507	1030	523
Dunton Mining Area	348	708	360
La Plata Mining Area	69	141	72
Watershed Background	827	919	92
Total	1814	3049	1235
Unallocated Reserve	778		
Loading Capacity	2592		

Table 5-2. Summary of Example TMDL Allocations and Needed Load Reductions (in g-Hg/yr) for Narraguinnep Reservoir

Source	**Allocation**	**Existing Load**	**Needed Reduction**
Wasteload Allocations	0	0	0
Load Allocations			
Atmospheric Deposition	9.2	36.8	27.6
Inter-basin Transfer from McPhee Reservoir	9.5	15.9	6.4
Watershed Background	8.6	25.4	16.8
Total	27.3	78.1	50.8
Unallocated Reserve	11.8		
Loading Capacity	39.1		

The analysis presented in this document has a significant amount of uncertainty, as discussed further in Section 6. The example allocations are believed to be conservative, because an unallocated portion of the TMDL is held in reserve. In addition, reduction in atmospheric deposition of mercury for the purpose of controlling direct deposition to the surface of the lakes may also result in a greater reduction in the watershed background mercury loading than can be attributed at this time.

Although estimates of the assimilative capacity and load allocations are based on best available data and incorporate a Margin of Safety, these estimates may potentially need to be revised as additional data are obtained. To provide reasonable assurances that the assigned load allocations will indeed result in compliance with the fish tissue criterion, a commitment to continued monitoring and assessment is warranted. The purposes of such monitoring will be (1) to evaluate the efficacy of control measures instituted to achieve the needed load reductions, (2) to document trends over time in mercury loading, and (3) to determine if the load reductions proposed for the TMDL lead to attainment of water quality standards. It is recommended that a detailed plan for continued monitoring be incorporated as part of the implementation plan for the TMDL.

6. Margin of Safety, Seasonal Variations, and Critical Conditions

6.1 Sources of Uncertainty

The analysis for this TMDL contains numerous sources of uncertainty, and load allocations must be proposed as best estimate "gross allotments" in keeping with the TMDL regulation at 40 CFR 130.2(g). Key areas of uncertainty have been highlighted in the Source Assessment and Linkage Analysis sections and are summarized below. The need for additional data collection, analysis, and modeling to reduce these areas of uncertainty will form the bulk of Phase II of this TMDL, which is outlined in Section 7.

The sources of uncertainty can be divided into two groups. The first group consists of sources of uncertainty that directly affect the ability of the linkage analysis to relate the numeric target fish tissue concentration to environmental mercury exposure concentrations in the Resrvoirs. These sources of uncertainty propagate directly to uncertainty in estimation of the loading capacity and TMDL. The second group consists of uncertainty in the estimation of external loads. These have their primary impact on allocations and affect the estimation of loading capacity only indirectly by causing a potential mis-specification in the data used for lake model calibration. The loading capacity estimate is much more sensitive to uncertainty in the first group and relatively robust to uncertainty in the second group.

The first group includes the following:

- Fish data from the Reservoirs are sparse. While the presence of problem concentrations of mercury in fish has been confirmed, the limited number of samples and collection times leads to uncertainty regarding the average population response as a function of fish weight/age.

- Even less data are available on small forage fish and invertebrates, which drive the food chain pathways leading to bioaccumulation in sport fish.

- Sediment mercury concentrations are characterized by a limited number of samples.

- Information on the vertical distribution of mercury in the water column and associated water chemistry is available for only two points in time (June and August 1999). Without additional sampling it is not possible to determine the extent to which these two times characterize the annual mercury cycle or whether 1999 conditions are representative of conditions in other years.

- Neither available resources nor available data allowed the development and calibration of a detailed lake mercury cycling model for Narraguinnep. Instead, the estimates of loading capacity for Narraguinnep are based on analogy to the McPhee model. Systematic differences may exist between responses in McPhee and Narraguinnep Reservoirs.

The second group includes the following:

- Watershed background loading of mercury is estimated using a simple water balance/sediment yield model. While the concentrations in tributary sediments are based on measured data, the estimated actual rates of movement of this sediment to the Reservoir are not constrained by field measurements at this time.

- Estimates of atmospheric wet deposition of mercury are based on a limited period of record at a site several hundred miles removed from the McPhee/Narraguinnep watersheds and using a relationship between mercury deposition and nitrate and sulfate deposition. Actual deposition of mercury at or near the Reservoirs has not been measured. Total mercury deposition to the watershed may well differ from the estimates used by a factor of 3 or more, based on best professional judgement of the authors.

- The extent to which atmospheric deposition of mercury onto the land surface contributes to watershed mercury loads is not known at this time, nor is the relative importance of local versus global mercury sources. Therefore, the benefit that might be obtained through reductions in mercury emissions from nearby power plants cannot be accurately determined.

One area in which the level of uncertainty is particularly acute is the estimates of atmospheric deposition of mercury. As described in Chapter 3, no direct measurements of atmospheric deposition of mercury are available at or near the Reservoirs. Estimates of deposition were made using nitrate and sulfate deposition as a surrogate. This procedure produces what appear to be reasonable results, but data are not available to confirm the estimates.

Fortunately, as described in Chapter 4, atmospheric deposition appears to account for a relatively small proportion (less than 10 percent) of the total mercury load to McPhee Reservoir. As a result, it is the opinion of the modelers that the uncertainty in the estimates of atmospheric deposition of mercury does not have a significant impact on the calibration of the D-MCM lake response model. This in turn means that the uncertainty in estimates of atmospheric deposition does not propagate significantly into estimates of assimilative capacity of the two Reservoirs.

Where the uncertainty in atmospheric deposition estimates does have a major impact is in the estimation of potential load allocations involving Narraguinnep Reservoir. This occurs because Narraguinnep, unlike McPhee Reservoir, appears to derive a significant amount of its total mercury load from atmospheric deposition. Current best estimates of mercury loads to Narraguinnep suggest that a significant reduction in atmospheric loading may be needed to achieve water quality standards.

The example allocations presented in Chapter 5 treat McPhee and Narraguinnep Reservoirs as a pair, and propose a large reduction in atmospheric loads to both Reservoirs to achieve standards in Narraguinnep. It is important to note that water quality standards in McPhee alone could apparently be achieved solely through reductions in watershed mercury loading, without reductions in atmospheric deposition of mercury.

The analysis of loading to Narraguinnep Reservoir suggests that existing watershed and inter-basin mercury loads slightly exceed the loading capacity for this waterbody, while atmospheric deposition of mercury is likely of the same order of magnitude as the watershed and inter-basin loads. This suggests that some reduction in atmospheric loading of mercury will likely be needed to meet standards in Narraguinnep. The magnitude of this reduction, however, is uncertain as a result of the uncertainty in the atmospheric deposition estimates. New data on atmospheric deposition of mercury in this part of Colorado, proposed to be collected at Mesa Verde National Park, should help to resolve this uncertainty.

There are thus many sources of uncertainty in the estimation of the mercury TMDL for McPhee and Narraguinnep Reservoirs. It is evident, however, that existing loads of mercury are too high to support designated uses, as shown by the tissue concentrations observed in fish.

Quantitative estimates are possible at this time for only some of the sources of uncertainty in the TMDL. It is also not appropriate to assume that all the sources of uncertainty are additive, since some sources will have positive or negative correlations with other sources. A full, quantitative analysis of uncertainty in the TMDL has not yet been feasible, but it might be appropriate as additional data are collected. The best professional judgment of the authors is, however, that there is a high probability that the true loading capacity of McPhee Reservoir lies within plus or minus 25 percent of the best estimates presented above.

Additional uncertainty is present in the estimates of loading capacity for Narraguinnep, as a complete lake model has not been constructed for this Reservoir. Given the near proximity of Narraguinnep to McPhee and the fact that water in Narraguinnep is primarily derived from diversions from McPhee, it is reasonable to assume that responses to loads in Narraguinnep will be similar to those in McPhee. Most important, it is assumed that fish body burdens in Narraguinnep will experience a near-linear response to declines in external mercury loads, as predicted by the McPhee model.

The TMDL regulation requires that estimates of loading capacity be made even where there is uncertainty in load estimates, and only "gross allotments" are possible for nonpoint loads. This report provides a best estimate from currently available data of the loading capacity for mercury, and the needed load reductions, for the two Reservoirs-but the uncertainty in these estimates is high. This uncertainty is addressed in part through use of a Margin of Safety (Section 6.2). The level of uncertainty, however, suggests the need for ongoing, adaptive management to meet water quality standards in the two Reservoirs. In particular, a monitoring program should be part of any implementation plan. Such a monitoring program would allow tracking of progress in attaining acceptable fish tissue concentrations in response to management actions. It would also provide the basis for potential revision (upward or downward) of the estimated load allocations consistent with attaining standards in the Reservoirs.

The uncertainty in the estimation of loading capacity and the TMDL could be reduced directly through collection of additional data to better characterize external loading rates, internal stores of mercury, and year-to-year variability in lake response. General monitoring recommendations appropriate to assess trends and refine estimates of loading and loading capacity include the following:

- Continue fish monitoring in the Reservoirs using a standardize sample collection protocol.

- Continue tributary mercury monitoring at key locations, including Dolores River near Dolores, key upstream tributaries draining mining areas, and the Lone Pine Lateral between McPhee and Narraguinnep.

- Establish a mercury deposition monitoring station near the Reservoirs as a part of the Mercury Deposition Network. Co-location of this station with the Mesa Verde NADP site is paramount. This site is near the Reservoirs but in the direction of the major power plants and provides a good database of nitrate and sulfate deposition data. In January 2002, an MDN site was established at the Mesa Verde location and is currently collecting data. This station follows the MDN protocol of monitoring wet deposition. While dry deposition is also important, methods for estimating dry deposition are not standardized and attempts to measure dry deposition should wait until the measurement methods move beyond the realm of research.

Uncertainty in the D-MCM modeling of mercury cycling within the Reservoirs could also be reduced through the following special-study efforts:

- Collect additional data on the mercury concentrations in biota, including lower trophic levels, and on seasonal and annual variability in concentrations.

- Collect higher-frequency data on thermal stratification and water chemistry within the lake, including mercury species, pH, chlorine, DOC, sulfur species, and particulate concentrations.

- Obtain better characterization of the particulate matter in the Reservoirs, including settling velocity and mercury sorption characteristics.

- Construct a site-specific lake response model for Narraguinnep Reservoir.

6.2 Margin of Safety

All TMDLs are required to include a Margin of Safety to account for uncertainty in the understanding of the relationship between pollutant discharges and water quality impacts. The Margin of Safety may be provided explicitly through an unallocated reserve or implicitly through use of adequately conservative assumptions in the analysis.

The example TMDL presented in Section 5 incorporates an explicit Margin of Safety as an unallocated reserve equal to 30 percent of the estimated loading capacity. As described in

Section 6.1, the margin of uncertainty about the estimated loading capacity is believed to be plus or minus 25 percent for McPhee and somewhat larger for Narraguinnep.

Uncertainty in the analysis for Narraguinnep is caused in large part by uncertainty in estimates of atmospheric deposition of mercury, including both the magnitude of wet deposition and the ratio of dry deposition to wet deposition. This uncertainty can only be addressed through the collection of deposition monitoring data and/or regional-scale modeling of mercury transport.

In sum, the example TMDL incorporates a Margin of Safety that is believed to account for uncertainty in the understanding of the relationship between pollutant discharges and water quality impacts. It is not, however, possible at this time to precisely estimate the magnitude of uncertainty in the estimation of lake loading capacities, particularly for Narraguinnep Reservoir. As a result, there is a small but non-zero potential risk that the proposed allocations will not result in achieving water quality standards.

6.3 Seasonal Variations and Critical Conditions

Federal regulations require consideration of seasonal variations and critical conditions in the estimation of a TMDL. The TMDL for McPhee and Narraguinnep is being developed to address fish tissue concentrations associated with bioaccumulation of mercury within McPhee and Narraguinnep Reservoirs, and there is no evidence of excursions of water quality standards for mercury. Because methylmercury is a bioaccumulating toxin, concentrations in tissue of game fish integrate exposure over a number of years. As a result, annual mercury loading is more important for the attainment of standards than instantaneous or daily concentrations, and the TMDL is appropriately expressed in terms of annual mercury loads. It is not necessary to address standard wasteload allocation critical conditions, such as concentrations under 7Q10 flow, because it is loading, rather than instantaneous concentration, that is linked to impairment.

The impact of seasonal and other short-term variability in loading is damped out by the biotic response. The numeric target selected is tissue concentration in piscivorus game fish of edible size, which represents an integration over several years of exposure, suggesting that annual rather than seasonal limits are appropriate. Nonetheless, the occurrence of loading that impacts fish does involve seasonal components. First, watershed mercury loading, which is caused by infrequent major washoff events in the watershed, is highly seasonal in nature, with most loading occurring during the early summer snowmelt period. Second, bacterially mediated methylation of mercury is also likely to vary seasonally. The timing of washoff events is not amenable to management intervention. Therefore, it is important to control average net annual loading, rather than establishing seasonal limits, in calculating the TMDL consistent with the existing loading capacity.

7. Additional Analysis and Characterization

As described in Section 1.6, this TMDL will be phased over time. The first phase consisted of initial data collection, analysis, and modeling that resulted in a rough estimate of mercury loading to the Reservoirs. Numerous data gaps and uncertainties in this estimation were identified throughout the report and summarized in Section 6. Section 7 describes Phase 2 of this TMDL, which identifies additional data collection and analysis efforts needed to minimize the uncertainties identified in Phase 1. As described in Section 6, the uncertainties identified in Phase 1 can be grouped into one of two categories: 1) estimation of the loading capacity of the Reservoirs; and 2) estimation of external loads.

7.1 Estimation of the Loading Capacity to the Reservoirs

Several areas of uncertainty were identified in estimations of loading capacity of the Reservoirs. The recommended additional sampling and analysis needed to address this uncertainty is outlined below:

1. Only a limited number of samples and collection times related to fish data were available for analysis in Phase 1. Additional data from both Reservoirs is needed to strengthen the population response component of the model, especially data related to fish weight, age, and trophic status.

2. Even less data are available on small forage fish and invertebrates, which drive the food chain pathways leading to bioaccumulation in sport fish.

3. Sediment mercury concentrations are characterized by a limited number of samples. Additional samples are neede to fill data gaps in both temporal and spatial scales.

4. Information on the vertical distribution of mercury in the water column and associated water chemistry is available for only two points in time (June and August 1999). Additional sampling is needed to determine the extent to which these two times characterize the annual mercury cycle or whether 1999 conditions are representative of conditions in other years.

5. Neither available resources nor available data allowed the development and calibration of a detailed lake mercury cycling model for Narraguinnep. Instead, the estimates of loading capacity for Narraguinnep are based on analogy to the McPhee model. Systematic differences may exist between responses in McPhee and Narraguinnep Reservoirs. Thus, modeling Narraguinnep Reservoir would help to decrease this area of uncertainty.

7.2 Estimation of External Loads

The 1999 sampling campaign for the McPhee watershed has enabled an initial estimate of mercury loading rates by sub-basin. The assessment, however, needs additional data to better focus in on the sub-watersheds generating significant sources of mercury load.

7.2.1 Watershed Sources of Mercury

Establishing new water and sediment sampling points will help indicate where the loads arise in the mining areas. Better and more place-specific estimates from these areas will provide the basis for field reconnaissance to identify specific source areas for potential remediation.

The previous (1999) sampling round provided a good start, but could not be comprehensive due to available LOE relative to the large size of the watershed. This work demonstrated that there is not one overwhelming source of mercury load; rather the watershed load appears to derive from multiple sources in the Rico, Dunton, and La Plata mining areas. Additional sample locations will further focus the assessment. For the Rico area, in particular, there is a lack of mainstem sampling stations that would help to determine in which areas the major loads arise.

To further refine the assessment, the next round of sampling should include several new sampling locations. In addition, key sampling stations evaluated previously should be re-sampled to confirm and refine previous estimates.Several new sampling locations are recommended. These are divided into several geographic areas:

Dolores River Mainstem/ Rico Mining District

The Dolores mainstem drains the Rico Mining District, which appears to be a major source of mercury load to McPhee. The 1999 sampling covered many of the smaller tributaries, but had no samples on the Dolores mainstem upstream of MCP-5, just above the confluence with the West Dolores River. Additional sampling points are needed in the mainstem to further constrain the areas of significant mercury loading. Recommended new sampling points (all of which appear to have potential road access) are:

1. Dolores River upstream of Barlow Creek north of Rico. This would provide a boundary condition for the area that appears to be upstream of the historic mining district.

2. Dolores River near settling ponds at Rico, upstream of Silver Creek.

3. Dolores River below Deadwood Creek, south of Rico and downstream of the historic mining area.

4. Stoner Creek above confluence with Dolores River. Stoner Creek enters the Dolores just upstream of existing station MCP-5 and is a major unmonitored sub-watershed. The uppermost reaches of Stoner Creek extend into the Rico mining district, so loading from this area should also be monitored.

West Dolores River

The 1999 sampling includes three stations along the West Dolores (MCP-4, MCP-19, and MCP-3), the first two of which bracket the heart of the Dunton Mining District. However, much of the mercury load appears to come from upstream of MCP-4, while additional load appears to arise downstream of MCP-19. Additional sampling is recommended at the following locations:

5. West Dolores River above Meadow Creek northeast of Dunton. This is upstream of MCP-4 and appears to be the limit of ready road access.

6. West Dolores River upstream of Groundhog Creek, downstream of Dunton. Some mining activity occurred in this area, downstream of MCP-19. A station here would help determine whether additional mercury load occurs in this area.

7. Groundhog Creek above confluence with West Dolores. Not known to be a mining area, but represents significant drainage that can perhaps be confirmed as not a significant source area.

La Plata Mining District
The headwaters of Bear Creek reach into the La Plata mining district. Samples at the mouth of Bear Creek (MCP-7) suggest a significant mercury load. An additional sample would be advisable upstream, near the mining area.

8. ? Upper Bear Creek. Depends on accessibility, which is not readily evident from topo maps.

Other Areas
The major drainage area that is lacking samples is Beaver Creek, which drains to the north side of McPhee. This drainage is estimated to contribute significant flow and sediment loading, so it would be advisable to determine the mercury content of the load.

9. ? Beaver Creek. Accessibility would need to be determined.

Re-sampling of Existing Stations
Of the stations sampled in 1999, those stations that are of key importance in evaluating sub-watershed loads should be resampled to confirm and refine previous estimates. The following seven stations are recommended for re-sampling:

1. MCP-3: West Dolores River near Mouth
2. MCP-4: West Dolores River above Dunton
3. MCP-5: Dolores River above West Dolores River
4. MCP-7: Bear Creek near confluence with Dolores River
5. MCP-11: Silver Creek near mouth
6. MCP-17: Dolores River at Big Bend Boat Launch
7. MCP-19: West Dolores River below Geyser Creek

7.2.2 Atmospheric Sources of Mercury

As discussed in Sections 3 and 6, the atmospheric loading model was based on surrogate analysis of sulfate and nitrate deposition at monitoring stations throughout the state. There were no actual measurements of mercury deposition, except for one station on Buffalo Pass in northern Colorado. Although the assumptions that formed the basis of this model are reasonable in terms of general depositional patterns in Colorado, there is a need to collect additional data specific to mercury deposition in the McPhee and Narraguinnep watersheds. Data specific to reducing uncertainty in this area is expected to come from three sources:

1. A mercury deposition monitoring station, as a part of the Mercury Deposition Network, has been established in association with the Mesa Verde NADP site. This site is near the Reservoirs and in the direction of the major power plants. Wet mercury depostion data has been collected at the site since January 2002.

2. Additional data on high-elevation snowpack analysis is expected to be forthcoming from the US GS. This information will help constrain the (winter) atmospheric loading component.

3. Sediment core samples from Narraguinnep – should this be included here???????